AGRICULTURAL RESEARCH INSTITUTE
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PROPOSED INTERNATIONAL RULES FOR NUMBERING ORGANIC RING SYSTEMS.

By AUSTIN M. PATTERSON

Preface.

IN 1921 the author suggested to the Board of Editors of the American Chemical Society that it might be advisable to publish a catalogue of organic ring systems with their systematic numberings. The Board decided that it would be, but felt it extremely desirable to secure beforehand a wide agreement among chemists as to the numberings.

Rules for numbering ring systems were drawn up and submitted to the Committee on Organic Nomenclature of the International Union of Pure and Applied Chemistry, consisting of A. F. Holleman (Netherlands) (*chairman*), A. J. Greenaway (Great Britain), Marquis (France), E. Paternò (Italy), A. Pictet (Switzerland), and A. M. Patterson (United States). They were also shown unofficially to the late Prof. Jacobson and to Dr. Stelzner, of Germany. Several drafts were made and much improvement resulted from the criticisms.

In their present form the Rules have been approved by the International Committee for a provisional period of two years, during which they will be open for the criticism of chemists generally. At the end of that period, if no fundamental objections are found to the Rules, the expectation is that they will be finally adopted for use in the journals of the respective countries, with any further improvements or corrections that may have been suggested.

Considerable time has been given to devising a set of Rules that shall be applicable to all systems of simple or fused rings and yet be as simple and clear as possible and preserve a maximum of the numberings now in use. The present article embodies the best results achieved to date. The ring systems described in Beilstein's "Handbuch," Richter's "Lexikon," Stelzner's "Literatur-Register," and the 18 volumes of *Chemical Abstracts* have been carefully checked and the numberings compared.

If and when the Rules are put into effect in the journals, they should be as free from causes for objection as they can be made.

It is urged that anyone having criticisms to make send them promptly to the author, or to his own representative on the International Committee. The question whether hydrogen atoms should be favoured for low numbers in all classes is an important one, and the recommendations of organic chemists are especially desired on this point (see " Position of Double Bonds," under *Comments*).

Publication of the catalogue of ring systems will be deferred, pending the final adoption of the Rules.

Rules and Notes.

Note 1. The word " system " is used to mean a single ring or a combination of rings united one to another by atoms common to both ("fused " systems). Rings united only by a valency bond as in diphenyl ($C_6H_5 \cdot C_6H_5$), or by an intermediate atom or chain as in diphenylmethane ($C_6H_5 \cdot CH_2 \cdot C_6H_5$), are not considered as parts of the same ring system for the purposes of these Rules.

Note 2. Derivatives. Although the following Rules determine the numbering of parent systems *in all degrees of hydrogenation*, it is not the intention to fix the position of hydrogen atoms in all their derivatives. All that is required of derivatives is *that their numbering conform to that of the lowest stage of hydrogenation of the parent system in Classes A II, B and C II, and to that of the saturated form in A I, C I, C III and D I.* For example, the Rules assign the positions 1–4 to the CH_2 groups in " tetralin," which numbering corresponds to the name 1 : 2 : 3 : 4-tetrahydronaphthalene. But this does not prevent the naming and numbering of a hydroxyl derivative of it as 5 : 6 : 7 : 8-tetrahydro-2-naphthol; the numbering of the latter is based on that of naphthalene, the least saturated form of the parent system. (Decision between two or more alternative numberings of derivatives in such cases is a separate matter lying outside the scope of the Rules.) Conversion of a derivative to the lowest stage of hydrogenation of the parent system may involve (1) replacement of substituting atoms or groups by hydrogen, (2) removal of hydrogen atoms in pairs, (3) removal of O_2, CH_3Cl, etc., from ring atoms if the latter can thereby pass to a well-recognised lower state of valence, (4) introduction of quinonoid structure, or rarely (5) conversion of tervalent into quinquevalent nitrogen. It should *not* involve the introduction of triple bonds, two double bonds attached to the same carbon atom, or new bridging bonds. In some cases there will be two or more isomeric least saturated forms which may equally well be regarded as the parent of the derivative.

Note 3. Lowest Numbers. The expression " lowest numbers," as used in connection with the Rules, signifies the numbers yielding

the smallest sum or, if the sums are equally small, those that include the lowest individual number or numbers. Thus, 1,3,5 is lower than 2,4,6; 1,4,5 is lower than 2,3,5; 1,2,5 is lower than 1,3,4; 1,1,3,4 is lower than 1,2,2,4.

A. The system consists of a single ring.
I. The ring is carbocyclic.

Rule 1. *Number around the ring in such a manner as to give to hydrogen atoms the lowest numbers possible.*

Examples :

(I.)   (II.)   (III.)   (Benzene) (IV.)
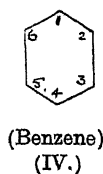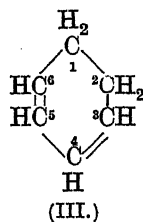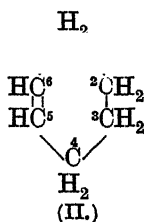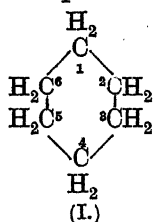
Note 4. Fixed orientations are an aid to memory and should not be neglected. Single rings should be oriented with Position 1 at the top and with the numbers proceeding clockwise around the ring.

II. The ring is heterocyclic.

Rule 2. *Choose as starting point a hetero atom of as high a group in the periodic table of the elements, and as low an atomic number in that group, as possible.*

Note 5. The following order as determined by the above rule, includes the commonly occurring hetero atoms : O, S, Se, Te, N, P, As, Sb, Si, Sn, Pb, Hg.

Rule 3. *With an atom of the preferred kind as 1, number around the ring in the way that gives to hetero atoms the lowest numbers possible.*

Rule 4. *Of two or more numberings conforming to Rules 2 and 3, choose the one that assigns low numbers most nearly in the order of precedence established in Rule 2.*

Rule 5. *Of two or more numberings conforming to Rules 2–4, choose the one that gives to hydrogen atoms the lowest numbers possible.*

B. The system contains at least two rings of five or more members, but no atomic bridges, crossed valence bridges or free spiro unions.

Note 6. An " atomic bridge " is one that contains atoms (*e.g.*, the bridge in norcamphane, V) as contrasted with a " valency

bridge " (*e.g.*, that in naphthalene, VI, or in norcarane, VII). The " peri " forms frequently encountered among aromatic compounds are included in Class B and are *not* treated as having an atomic bridge, although strictly speaking they do contain one. For example, acenaphthene, VIII, is a " peri " form. Such forms may be regarded as resulting from three ordinary or " ortho " fusions : A with B, B with C, and A with C.

(V.)   (VI.)   (VII.)   (VIII.)
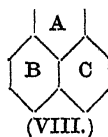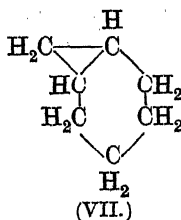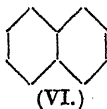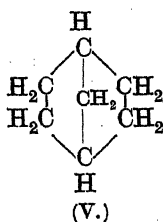
Note 7. " Crossed valency bridges " are valency bridges that are represented by the plane formula as crossing each other, as shown in Example XLVIII.

Note 8. A " spiro union " is one formed by a single atom which is the only common member of two rings. A " free spiro union " is one constituting the *only* union, direct or indirect, between two rings, as in IX. Systems in which the rings are united in some other way (that is, by intermediate rings) as well as by the spiro union are not necessarily excluded from Class B.

(IX.)
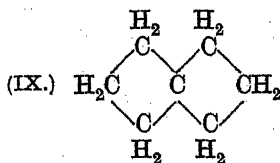
Note 9. In determining whether or not a system contains at least two rings of five or more members, one counts as component rings *only the smallest number of smallest rings that together will account for all the atoms and valencies*. Thus, in Example VII it is possible to see a 3-ring, a 6-ring and a 7-ring, yet it is called a " 3,6 " system because the 3-ring and the 6-ring together account for all the atoms and valencies and the 7-ring is merely the circumference of the fused 3- and 6-rings; the system does not belong in Class B. Valency bridges which are sometimes used to account for the chemical peculiarities of a compound but which are not absolutely indispensable in representing the formula are not considered in these Rules. The bridge sometimes shown between N and CH in one formula for anthranil (X) is a case in point, for a formula may be

written for it without this bridge, as in XI : it is therefore classed as a 5,6 system and placed in Class B. The middle bridge sometimes shown in the formula for anthracene is another example. Anthracene is treated not as a 4-ring system (XII) but as a 3-ring system (XIII).

(X.) (XI.) (XII.)
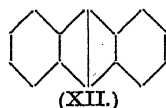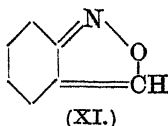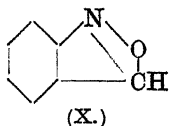
Rule 6. Orient the formula so that the greatest possible number of rings will be in a horizontal row.

Note 10. Triangles in such a row should have one side vertical, other rings two sides vertical (this requires a deformation of the polygons with an odd number of sides, thus: △ or ⬠). Accordingly, hexagons should have angles, not sides, at top and bottom. Anthracene (XIII) constitutes a horizontal row of three, so do fluorene (XIV) and *s*-indacene (XV); but phenanthrene (XVI) does not.

(XIII.) (XIV.) (XV.) (XVI.)
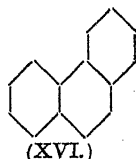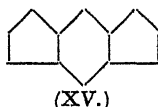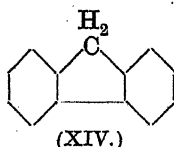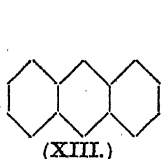
Rule 7. Of orientations conforming to Rule 6, choose the one that places as many as possible of the remaining rings above and to the right.

Note 11. Only the *number* of rings, and not their size or distance from the centre, is taken into account. When the correct orientation is not immediately apparent, bisect the " horizontal row " by a horizontal axis and a vertical axis (as in XXI) and count the rings and fractions of rings in the four quadrants. If there is more than one combination of rings that could serve as the " horizontal row," apply the bisection in the other cases also (as in XXII). Choose the orientation that has as many as possible of the " remaining rings " in the upper right quadrant; if two or more orientations meet this requirement, choose the one of them that has as few rings as possible in the lower left quadrant. In the examples, phenanthrene (XVI) is shown correctly oriented with its single " remaining ring " turned upward toward the right; triphenylene (XVII) has one in the upper right quadrant and one in the lower right; Examples XVIII–XX show right and wrong orientations of chrysene; and

XXI and XXII show right and wrong orientations in a case that might not be immediately apparent.
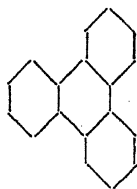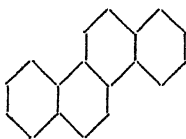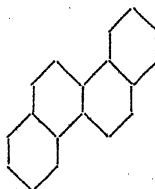
(XVII.)   (XVIII.) (right)   (XIX.) (wrong)   (XX.) (wrong)
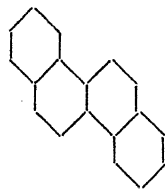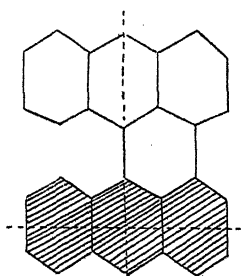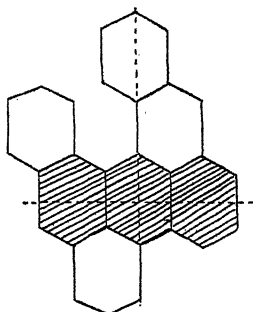
(XXI.) (right)   (XXII.) (wrong)

Rule 8. Of orientations conforming to Rules 6 and 7, choose the one that gives the lowest numbers to hetero atoms when the formula is numbered as directed below (Rule 12).

Examples :
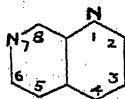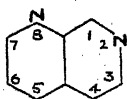
(XXIII.) (right)   (XXIV.) (wrong)   (XXV.) (right)   (XXVI.) (wrong)
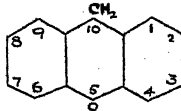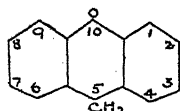
Rule 9. Of orientations conforming to Rules 6–8, choose the one that assigns low numbers to hetero atoms most nearly in the order of precedence given in Rule 2.

Examples :
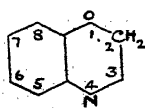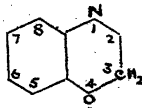
(XXVII.)   (XXVIII.)
(right)   (wrong)

Rule 10. Of orientations conforming to Rules 6–9, choose the one in which unnumbered carbon atoms follow the lowest numbers possible.

Examples : In XXIX the unnumbered carbon atoms follow the numbers 4,4,8,9; these are lower than the 4,5,9,9 of XXX. Similarly, the numbers 2,5,8 of XXXI are lower than the 3,5,8 of XXXII.
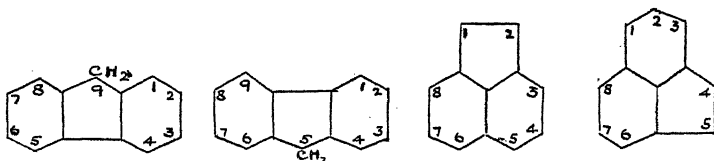
(XXIX.) (right)　(XXX.) (wrong)　(XXXI.) (right)　(XXXII.) (wrong)

Rule 11. Of orientations conforming to Rules 6–10, choose the one that gives to hydrogen atoms the lowest numbers possible.

Rule 12. Number the oriented formula by beginning with the first free angle of the upper right ring and proceeding clockwise around the entire formula to the beginning, numbering all carbon atoms that are not common to two or more rings, and all hetero atoms. Number interior hetero atoms last of all, following the shortest path from the highest previous number.

Examples : (See also XXIII–XXXII)

(XXXIII.)　(XXXIV.)
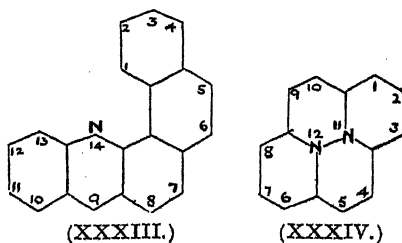
Note 12. The " first free angle " is the first angle, not also part of another ring, from which one may proceed clockwise around the ring.

Note 13. The " upper right ring " is the highest ring in the formula or, if two or more are equally high, then the ring farthest to the right in the highest row.

Note 14. Ordinarily, no numbers are needed for carbon atoms that are common to two or more rings. When such a need does arise, it is recommended that they be numbered by adding *a* (or *b, c,* etc., in case of a succession of them) to the number of the

position just preceding in the clockwise order; interior carbon atoms are considered to follow the highest number.

Examples :
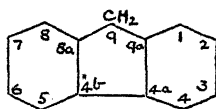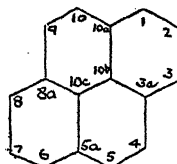
(XXXV.)   (XXXVI.)

Note 15. Formulæ should always be represented in their correct orientation, because the maintaining of a fixed position is a valuable aid to memory. If one has a mental picture of the oriented formula, one can readily renumber it at any time by Rule 12.

C. The system does not belong to Classes A and B, and does not contain free spiro unions.

I. The system consists of two rings only, separated by either an atomic bridge or a valency bridge.

Note 16. Formulæ of systems belonging to Class C 1 must be drawn so that the bridge contains as few members as possible.

Examples :
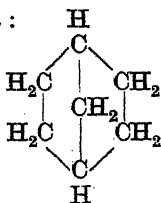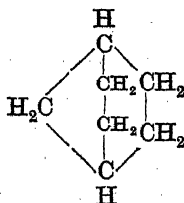
(XXXVII.) (right)   (XXXVIII.) (wrong)

Rule 13.   Starting with one end of the bridge as 1, number around the longer way to the other end of the bridge, then on around the shorter way to the beginning, and finally, by the shortest path, along the bridge itself if the bridge is atomic. If there are two or more possibilities for the shortest path, choose the shortest path from the highest previous number that will give a decision. Number all ring members.

Examples :
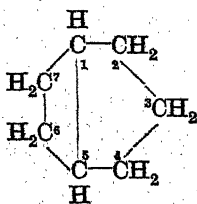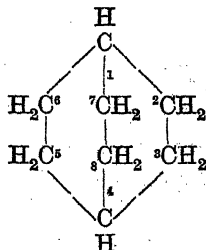
(XXXIX.)   (XL.)

Rule 14. *Of numberings conforming to the above rule, choose the one that gives the lowest numbers to hetero atoms.*

Examples :
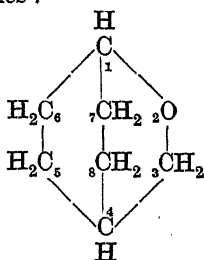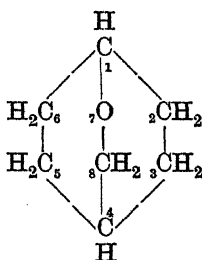
(XLI.) (right) (XLII.) (wrong)

Rule 15. *Of numberings conforming to the above rules, choose the one that assigns low numbers to hetero atoms most nearly in the order of precedence given in Rule 2.*

Rule 16. *Of numberings conforming to the above rules, choose the one that gives to hydrogen atoms the lowest numbers possible.*

II. The system contains one or more atomic bridges the removal of which would throw the system into Class B.

Rule 17. *Disregarding the atomic bridges and converting the resulting form to the lowest state of hydrogenation, number by Rules 6–12; then number the bridge members, following the shortest path as in Rule 13.*

Examples :
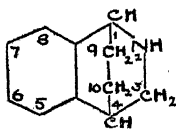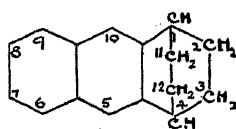
(XLIII.) (XLIV.)

Note 17. The atomic bridges in Class C II must contain as few members as possible and, the number of members having been determined, as few hetero atoms as possible. After the outside numbers have been determined by Rules 6–12, the formula must be so oriented that the ends of the atomic bridges receive the lowest numbers possible. For example, Formula XLIII is so drawn that the NH group is part of an outside ring and not of the bridge, so that it may receive as low a number as possible. In XLIV the bridge is shown between positions 1 and 4, not between 6 and 9.

For conversion to the lowest stage of hydrogenation, see Note 2.

III. The system does not belong under I or II.

Note 18. The systems of Class C III contain two or more bridges, either atomic or valency. Special care must be taken to draw the formula so that the bridges shall be as simple and of as few members as possible. A branched bridge is regarded as consisting of a main bridge and one or more branch bridges. A branched bridge should be preferred to crossed bridges even though it contains more members (see XLVII and XLVIII), but in no case should the chain of bridge members between the two bridge ends be greater than either of the outside chains between the same points. In difficult cases it may be advisable to construct a spatial model so as to decide upon the most natural plane formula.

Examples :
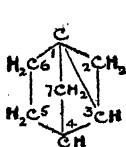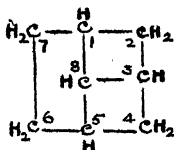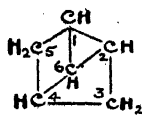
(XLV.) (XLVI.) (XLVII.) (right) (XLVIII.)
(wrong)
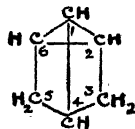
> *Rule 18. Select as the chief bridge (one end of which becomes position 1) the one having the most members or, if two have an equally large number of members, the one that divides the outside ring more symmetrically ; then number as in Rule 13 ; then number any remaining bridge members by the shortest path.*

Examples : See XLV, XLVI, XLVII.

Note 19. If a branched bridge is present, part of it may constitute the chief bridge; for example, in XLVI, 1–8–5 is the chief bridge and 3–8 is the other bridge.

> *Rule 19. Of two or more numberings conforming to Rule 18, choose the one that gives the lowest numbers to the ends of the other bridges.*

Example : See XLV.

> *Rule 20. If two or more numberings are possible in conformity with Rules 18 and 19, apply Rules 14–16.*

D. The system contains one or more free spiro unions.

I. The system contains spiro unions only.

> *Rule 21. Beginning with a ring member next to the spiro atom in the right end ring, number clockwise around the end*

ring and on around the entire formula. Number all ring members.

Example :

(XLIX.)
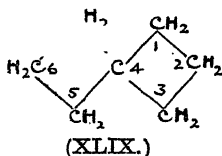
Rule 22. *Of two or more numberings conforming to Rule 21, choose the one that gives the lowest numbers to spiro atoms.*

Rule 23. *If there are two or more numberings conforming to Rules 21 and 22, apply Rules 14–16.*

Examples :

(L.)   (LI.)
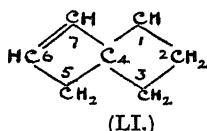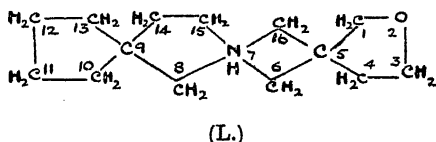
II. The system contains other ring unions in addition to spiro unions.

Rule 24. *(Provisional.) Treat separately each complex united by a free spiro union to another complex, giving to each the numbering it would have separately under the foregoing rules, but distinguishing the numberings from one another (as by primes). Give to the spiro atoms as low numbers in each complex as is consistent with the numbering of that complex.*

Example :

(LII.)
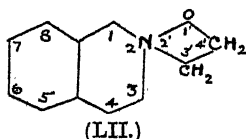
Comments.

Position of Double Bonds.—Opinions of chemists are divided as to whether saturated or unsaturated linkings should be given the preference in assigning low numbers. Usage in the past has apparently favoured one practice for certain classes of rings and the reverse for certain others. There seems to be a feeling that practice should be uniform and the Rules as now formulated favour saturated

linkings for low numbers in all classes. This number accords with such names as 1 : 2-dihydrobenzene, 1 : 2 : 3 : 4-tetrahydronaphthalene and 1 : 2-pyran, but not with such as 1-*cyclo*pentene and Δ²-pyrroline.

To favour *un*saturated linkings for low numbers in all classes would, in the opinion of the author, be less satisfactory. The fact is, that in certain classes compounds are usually named on the basis of parent forms low in hydrogen (as with furan, anthracene), while in others the compounds are usually named on the basis of saturated parent forms. Hence in the former classes the names tend to give low numbers to hydrogen atoms (as with 1 : 2-pyran, 1 : 2-dihydroanthracene), while in the latter classes the names tend to give low numbers to double bonds (as with 1-*cyclo*pentene, 1-*spiro*heptene). The two systems overlap in such cases as 1 : 2 : 3 : 4-tetrahydrobenzene (1-*cyclo*hexene). Perhaps the Rules should recognise and embody this contrast. However, if chemists are willing to use such names as 4-*cyclo*pentene and 6-*spiro*heptene, or to adopt some other way of expressing the high numbers of the double bonds in these compounds, the present Rules ought to work satisfactorily. They at least have the merit of being simpler thus, but an ideal solution has not yet been attained.

Numbering of Classes A and B.—The principles employed in numbering systems of these classes are in general those used in M. M. Richter's "Lexikon der Kohlenstoffverbindungen" (see pages 14–26 of the introduction to the third edition); but inconsistencies have been eliminated and all hetero atoms are required to be numbered. Of the 311 numbered formulæ of Classes A and B given by Richter, 73 per cent. conform to the Rules; if Richter had numbered all hetero atoms, 88 per cent. would have conformed.

If the Rules are applied without exception, the commonly accepted numbering of a few well-known parent forms, including anthracene, phenanthrene, acridine, xanthene and purine, will have to be changed. Serious consideration has been given to introducing special rules in order to preserve some of these accepted numberings, and also to making outright exceptions of them. The overwhelming sentiment of organic chemists who have been consulted has, however, been in favour of keeping the Rules as simple as possible and making no exceptions. An elaborate attempt has been made by Stelzner and Kuh (see the 99-page article in the introduction to Vol. III of Stelzner's "Literatur-Register") to extend the principle of the commonly accepted numbering of anthracene and phenanthrene to other polycyclic systems. It leads to hopeless complications.

Definition of Class B.—This class includes the large majority of all known organic ring systems, and most of the compounds represented

by them are of the aromatic type. The definition is so drawn as to exclude such systems as norcarane, bi*cyclo*[3,1,0]hexane, etc., which are customarily numbered as systems of Class C. Any distinction between Classes B and C must be more or less arbitrary, but the line drawn in the Rules conforms fairly closely to actual usage. It would be more consistent to number the systems of Classes B and C alike and to include all ring members in the numbering, but this would run the numbers up very high in polycyclic aromatic compounds, and for the most part these additional numbers would not be used.

Numbering of Class C.—The method of numbering the bridged systems of Class C follows that of von Baeyer (*Ber.*, 1900, **33**, 3771–5), but extends it to cover many possibilities which von Baeyer did not attempt to consider. Class C II includes certain bridged systems (about forty are actually known) which are most conveniently numbered by treating them as Class B forms to which bridges have been attached.

Numbering of Complex Spiro Systems.—Rule 24 has been marked "provisional" because at some later time it may be thought desirable to give directions for numbering these systems, "straight around" like the preceding classes. No simple and certain way of doing this has as yet been worked out.

Additional Examples.

The following additional examples have been appended at the request of the International Committee for the purpose of showing more clearly the application of the Rules. In Classes C II and C III the chief bridge is denoted by a heavy line. "B_3" refers to Beilstein, 3rd edition; and "Richter" to M. M. Richter's "Lexikon" ("Ringsysteme" in Vol. I).

ADDENDUM.—The Publication Committee of the Chemical Society directs attention to three papers in the Journal of the Indian Institute of Science, Vol. **7**, Part VIII, pp. 145–195 :

1. "The Systematic Nomenclature of Polycyclic Carbon Systems." By J. J. Sudborough.
2. "Polycyclic and Cage Systems of Carbon Compounds." By J. J. Sudborough and P. Ramaswami Ayyar.
3. "The Systematic Nomenclature of Heterocyclic Compounds including Polycyclic Structures." By J. J. Sudborough.

14

CLASS A I

cyclo Propene   cyclo Butadiene   cyclo Butene   cyclo Pentadiene   cyclo Pentene   cyclo Heptatriene (Tropilidene)

CLASS A II

Ethylene oxide   iso Thioxazole   Furazan   1:2:3-Triazole   2:1:3-Triazole   1:2:4-Triazole

1:2:3-iso Triazole   Oxazole   Iminazole (Glyoxaline)   Pyrazole   1:3-Thioxole   Pyrrole

Δ²-Pyrroline   iso Pyrrole   1:2:3:6 Dioxdiazine   1:4:2:5-Oxtriazine   as-Triazine   o-iso Oxazine

Pyrimidine   4:5-Dihydropyrimidine   Pyridine   3:4-Dihydropyridine   1:2-Pyran

CLASS B

bicyclo[3,3,0]Octatetrene   1:2:3-Benzotriazole   Anthranil   Purine

Pyrrocoline   Benzofuran (Coumarone)   Indene   Quinazoline

Naphthyridine   Quinoline   Naphthalene   ββ-Naphthoxazole

Carbazole

Phenoxazine

Phenazine
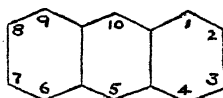
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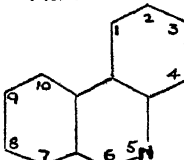
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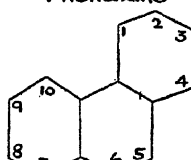
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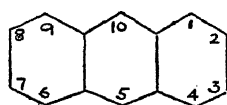
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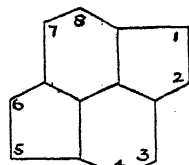
Pyracene
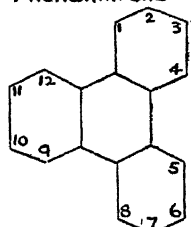
Triphenylene

Quiniminazole
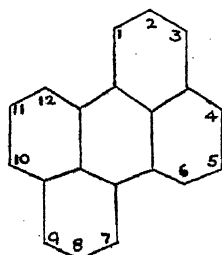
Perylene

Picene

Pyranthene
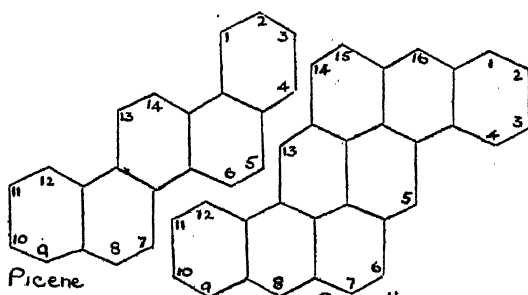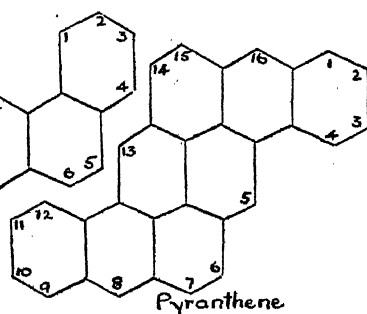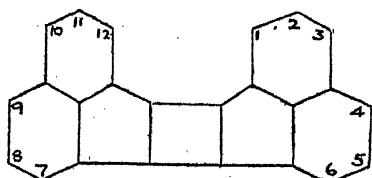
Heptacyclene
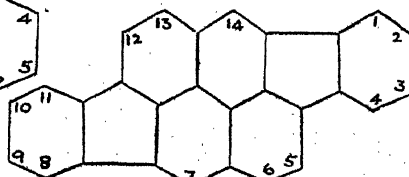
Inariene
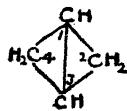
CLASS CI
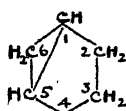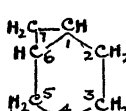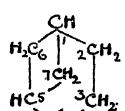
bicyclo[1,1]Butane. bicyclo[3,1,0]Hexane. bicyclo[4,1,0] Heptane (Norcarane) bicyclo[3,1,1] Heptane (Norpinane) bicyclo[2,2,1]Heptane (Norcamphane)
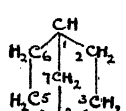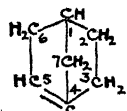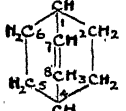
bicyclo[2,2,1]Hept-4-ene. bicyclo[2,2,2] Oct-7-ene B_3 IV, 715 Nortropidine p-Benzene-diazoimide
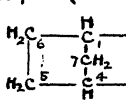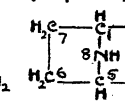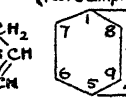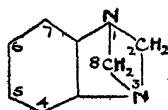
CLASS CII
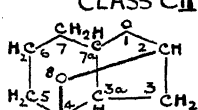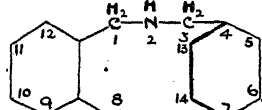
B_3 IV, 567 B_3 III, 596 B_3 II (1096)

CLASS CIII
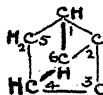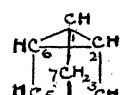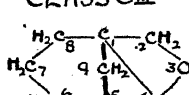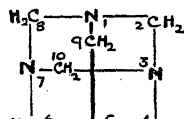
B_3 I (266) Tricyclo[2,2,1,0²·⁶]-Heptane B_3 III (460) Hexamethylenetetramine

CLASS DI
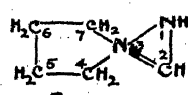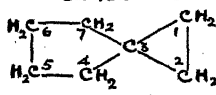
B_3 IV, 958 as-spiro Heptane. Oxetone
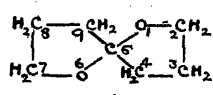
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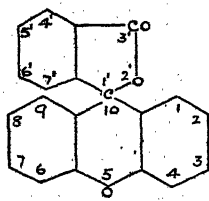
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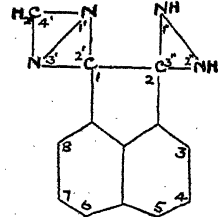
I.—*The So-called Poisoning of Oxidising Catalysts.*

By CHARLES MOUREU and CHARLES DUFRAISSE.

1. DAVY (*Phil. Trans.*, 1817), in his remarkable investigations on flames, observed that certain combustible gases (especially olefiant gas) prevent hydrogen from burning in oxygen under the influence of an electric spark. Turner (*Edinburgh Phil. Journ.*, 1824, **11**, 99) and W. Henry (*Phil. Trans.*, 1824, Part II, p. 266), working independently, found that these same gases had the property of preventing the combustion of hydrogen in the presence of finely-divided platinum; this was the first observation of the " poisoning " of a catalyst. Faraday (*Phil. Trans.*, 1834, Part I, p. 71) repeated these experiments and extended them to other gases or vapours. Similar observations were made also by W. C. Henry (*Phil. Mag.*, 1836, [ii], **9**, 324). These phenomena are closely related to more recent observations, *e.g.*, the action of gases such as acetylene, hydrogen sulphide, and hydrogen phosphide, in hindering the catalytic oxidation of ammonia gas in the presence of platinum (Decarrière, *Compt. rend.*, 1921, **172**, 1663; 1921, **173**, 148; 1922, **174**, 460).

How should these phenomena be interpreted? Various hypotheses have been postulated, but, as Faraday justly observed, they are not satisfactory. The explanation which is most commonly given even now consists in supposing that there is a modification of the catalyst, although this idea was rejected by Faraday as a result of some very conclusive experiments. Indeed it is difficult to see any essential difference between the experiments of Davy, in which a spark was used, and those of Turner and Henry, in which finely-divided platinum was used as a catalyst. The same materials were used in both and the same hindering action was observed; it is therefore probable that the mechanism of the action is analogous in the two cases. Since, however, we cannot reasonably speak of

" poisoning " an electric spark, it is advisable to reject this term altogether, as tending only to perpetuate an erroneous idea of the true mechanism of the action. For the same reason, we may also reject the interpretation, which consists in supposing the formation on the surface of the catalyst of a protecting layer which would insulate it from the gaseous mixture. This explanation is not very satisfactory even for experiments with a catalyst, and it is meaningless in the case of Davy's work, with an electric spark and no catalyst. It is necessary, therefore, as Faraday has already insisted, to look for some other explanation.

2. We propose to interpret these phenomena by means of a theory developed by us in order to explain our own observations of the hindering of oxidation, which may be summarised as follows :

Certain compounds, if added in very small quantities to autoxidisable substances, prevent their autoxidation. We have named these compounds " antioxygenes " (*Compt. rend.*, 1922, **174**, 258). Compounds having one or more phenolic hydroxyl groups always possess this property toward a large number of autoxidisable substances, and sometimes to a very high degree ; thus quinol, catechol, and pyrogallol are particularly active in this respect. In our opinion (*ibid.*, 1923, **176**, 624), the mechanism of this action is as follows : The antioxygenes act by decomposing catalytically the peroxide $A[O_2]$,* which results from the union of the autoxidisable substance with one molecule of free oxygen, O_2. The peroxide $A[O_2]$ oxidises the antioxygene B with the formation of the peroxide $B[O]$, whilst it is transformed itself into another peroxide, $A[O]$. The two peroxides, $A[O]$ and $B[O]$, as they are antagonistic, mutually destroy each other (as has been observed in the case of a number of antagonistic peroxides) and thus regenerate the three molecules, A, B, and O_2, in their original state. The three equations below sum up our conception of the antioxygenic action :

$$A + O_2 = A[O_2]; \quad A[O_2] + B = A[O] + B[O]; \quad A[O] + B[O] = A + B + O_2.$$
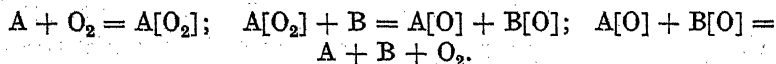
Numerous conclusions may be predicted as a result of this theory, *e.g.* :

(i) Antioxygenic properties can belong only to oxidisable substances.

(ii) Antioxygenic properties should increase with the affinity of B for oxygen. There must, however, be an upper limit, which depends, among other conditions, on the ability of the autoxidisable substance A to be oxidised.

* The brackets are used to indicate that the oxygen is active.

(iii) Every oxidisable substance should show some antioxygenic properties, although the circumstances in which these are most strongly developed may vary according to the nature of the substance selected.

(iv) A given catalyst, B, should be able to function either as a positive catalyst or as a negative one, the direction of the catalysis being positive if the peroxide B[O] attacks the substance A in preference to the peroxide A[O], and negative if the converse conditions prevail:

$$A + O_2 = A[O_2]; \ A[O_2] + B = A[O] + B[O]; \quad \begin{array}{l} \xrightarrow{\text{Positive}}_{\text{Catalysis}} \ \begin{array}{l} B[O] + A = B + A[O]; \\ A[O] \longrightarrow \text{stable AO} \end{array} \\ \xrightarrow{\text{Negative}}_{\text{Catalysis}} \ B[O] + A[O] = A + B + O_2 \end{array}$$
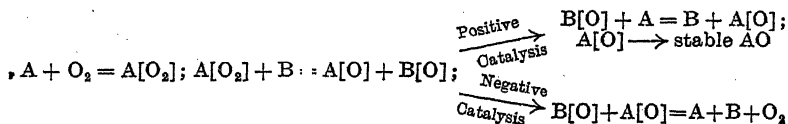
In some cases, moreover, we must expect that the same catalyst may function sometimes as a negative, and sometimes as a positive catalyst, as a result of imperceptible variations of conditions.

It is well to add that this theory, which we have used as a guide in our researches for several years past, has not only enabled us to account for all the facts already known, but also to foresee others which, but for it, would have been entirely unexpected, e.g., the catalytic properties of iodine and its compounds, of sulphur and its compounds, etc. (Compt. rend., 1923, **176**, 797; 1924, **178**, 824, 1862). We consider that this theory can also account easily for the results obtained by Turner and Henry. We assume that the catalysis of the oxidation of hydrogen in contact with platinum occurs because of the formation of an unstable platinum oxide, $Pt[O_2]$. The gas which hinders this reaction may play the part of an antioxygene toward this transitory oxidation of the platinum, just as quinol, for example, plays the part of an antioxygene in the oxidation of benzaldehyde by interfering with the fixation of free oxygen by this compound. The catalysis may be represented by the following system of three equations, in which B represents the gas which prevents the reaction.

$$Pt + O_2 \quad = Pt[O_2]$$
$$Pt[O_2] + B \quad = Pt[O] + B[O]$$
$$Pt[O] + B[O] = Pt + B + O_2$$
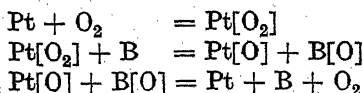
As the platinum oxide is destroyed catalytically as fast as it is formed, the platinum is thus deprived of its catalytic power of oxidation.

It could also be supposed that the platinum, acting as an oxygen carrier, oxidises the hydrogen and the interfering gas simultaneously

to form two antagonistic peroxides, which then are mutually reduced by each other, in conformation with the usual reaction.*

The so-called poisoning of the catalyst may therefore be in reality nothing but an antioxygenic action, just as in our experiments. In support of this point of view, it is important to observe that the gases indicated as having this hindering action are without exception oxidisable, as our theory requires. Indeed, W. Henry had already noted in 1824 (*loc. cit.*) that hindering properties were not to be found in "gases which do not combine with oxygen," and Faraday's researches fully confirmed this observation.

We consider that our theory applies similarly to the various cases of catalytic poisoning in oxidation phenomena.

As for Davy's experiment, we have here an ordinary antioxygenic action, as in our own experiments : the hydrogen is the oxidisable substance A and the interfering gas (ethylene, carbon monoxide, etc.) plays the part of the antioxygene B.

In conclusion, it is of interest to notice how complex may be the chemical phenomena which take place in a reacting mass, even although the final effect, the only one which we perceive, is relatively simple. We are, indeed, being compelled more and more to adopt the view that a chemical reaction is in reality made up of a series of transformations of different rapidities. Of these we observe only the final one, which corresponds to a stage possessing a greater stability than those preceding it.

LABORATOIRE DE CHIMIE ORGANIQUE,
    COLLÈGE DE FRANCE, PARIS.   [*Received, June 18th, 1924.*]

II.—*A Fractionating Column with Moving Parts.*

By JAMES ECKERSLEY MYERS and WILLIAM JACOB JONES.

CONSIDERABLE attention has been paid to the improvement of the fractionating column and to the question of its efficiency. The matter is fully treated in " Distillation Principles and Processes " by Sydney Young (London, 1922) and in the " Symposium on

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* It has sometimes been observed that the catalyst appeared to have lost its catalytic activity after it had been subjected for a moment to contact with a reacting mixture contaminated with certain interfering gases, as in the case, for example, of contamination by hydrogen phosphide. Here we must admit that the interfering gas has caused the formation (by oxidation or by condensation or by reaction on the catalyst) of substances of small volatility, which remain fixed on the surface of the catalyst and must be destroyed in order that the catalytic activity (regeneration of the catalyst) may reappear. These substances then play the part of antioxygenes in accordance with the general mechanism explained above.

Distillation " (*J. Ind. Eng. Chem.*, 1922, **14**, 476—497). However, the columns therein described are of the usual type with stationary parts, and it was suggested to the authors by Professor Arthur Lapworth, F.R.S., that it would be of interest to construct a fractionating column with moving parts and to compare its performance with those of fractionating columns of the usual type.

In the perfect fractionating column equilibrium between vapour and liquid would be attained at each point or in each section. For such an arrangement a necessary condition would be perfect contact between vapour and liquid at each point or in each section throughout the column. The more nearly this is approached in real practice, the greater will be the efficiency. In order to attain this, agitation of the vapour and a continuous fine dispersion of the liquid in each section of the column would be helpful, provided, of course, that the energy consumed in effecting these two operations was not excessive. In the case of an upright column of cylindrical or conical form, and consisting of several sections, the mechanically simplest way to effect fine dispersion of the liquid in each section is to provide the column with a central vertical revolving shaft, which within each section carries a horizontal and centrally-placed disk or cup, the function of the revolving disk or cup being to receive the liquid falling from the next higher section, and by centrifugal action to impel it either in the form of fine drops or as a thin film through the section.

In its flight the liquid comes into intimate contact with the ascending vapour in the section. After its flight the liquid falls in contact with the wall of the section, and finally, when it arrives at the aperture in the bottom of the section, drops down on to the revolving disk in the next lower section, where the process above described is repeated. In order to secure the greatest efficiency the duration of free flight should be considerable compared with the time occupied in falling in contact with the wall, and for this reason a cup form of impeller would in general be preferable to a disk one, as the former would give an initially upwardly-directed flight with a consequently lengthier trajectory for a given free horizontal range. However, in practice with the forms and dimensions of column and at the speeds of revolution which we have employed, we have found no advantage in the use of a cup form over a disk one. In this connexion it appears that it is neither the exact shape of the disk nor the speed of revolution of the shaft that matters so much as the peripheral velocity of the disks. Therefore, by using disks of greater diameter the same effect could be attained with a diminished speed of revolution of the shaft, and this would be a considerable engineering and economic consideration in the

practical employment of a rotary column, but in any case an adequate period of free flight must be given to the liquid.

Agitation of the vapour in each section could be effected by means of propeller blades, of suitable form and dimensions, fixed to the shaft and placed below the disk. In the experiments described below, however, we have not employed such a vapour-agitating device.

FIG. 1.

7 CHAMBERED ROTARY STILLHEAD.
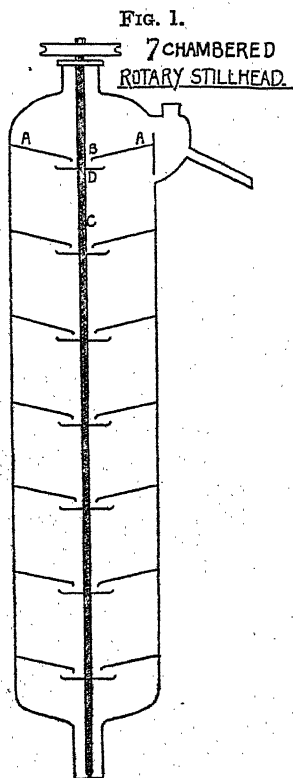
We have designed a fractionating column on the lines described in the foregoing. The column, a skilful piece of work by Mr. Stelfox of Manchester, was constructed of tinned copper, and was cylindrical in form, 32·5 cm. high and 7·5 cm. in diameter. It was divided into seven sections by downwardly-directed conical trays, A, which were equally vertically spaced at 3·5 cm., and the centres of which were circular horizontal apertures, B, 1·25 cm. in diameter. A shaft, C, made of thin iron rod, passed centrally through the apertures, and at its end at the bottom of the column worked on a bearing which was fixed to the column. Within each section the shaft carried a thin copper horizontal disk, D, 2·5 cm. in diameter. In order to secure the best working it is important that both column and shaft should be accurately vertically orientated. The shaft emerged out of the highest section by a fairly tightly stuffed passage, and, above, it carried a driving pulley. The highest section of the column was provided with a side exit-tube for the vapour, and near by was a thermometer to register the temperature of the escaping vapour. The whole column was protected from draught by an asbestos sheet.

In an experiment the liquid mixture to be fractionally distilled was contained in a copper boiling flask, which was attached by means of a cork to the bottom of the column. The driving pulley was attached to a motor and to a tachometer. The vapour issuing out of the exit-tube was condensed, collected in a receiver, and thereafter examined. Throughout all our trials a constant rate of collection of distillate was maintained, the heating being so controlled that about one drop of distillate fell per second into the

receiver. In our experiments the atmospheric pressure was sufficiently near normal to obviate any correction of boiling points on that account. By conducting our distillations under the described conditions, we were enabled directly to compare the results obtained with our column with those obtained with other columns on identical mixtures at the same rate of distillation. In each experiment, 200 c.c. of mixture were used. In the tables the following abbreviations are used. F T stands for the final temperature of the fraction, V for the volume of the fraction in c.c., V/D for the volume of the fraction per degree, T V for the total volume of distillate, and R for the number of revolutions of the shaft per minute.

Experiment A. The mixture consisted of equal parts by volume of benzene and toluene.

Experiment B. The mixture consisted of equal parts by volume of benzene and toluene.

FT.	V.	V/D.	TV.	R.	V.	V/D.	TV.	R.
82°	41	22·8	41	1100	81·0	45·0	81·0	1600
84	40	20·0	81	1100	4·5	2·3	85·5	2400
86	8	4·0	89	1200	6·0	3·0	91·5	2400
88	7	3·5	96	1400	3·0	1·5	94·5	2400
100	13	1·1	109	1400	6·5	0·5	101·0	2400
108	12	1·5	121	1500	10·0	1·2	111·0	2400
110	42	21·0	163	1500	20·0	10·0	131·0	2400

Comparison of these two experiments shows the effect which an increased speed of rotation, and therefore finer dispersion of the liquid in the column, has on the completeness of the separation into the constituents.

Experiment C. The mixture distilled contained 99 c.c. of ethyl alcohol and 101 c.c. of water. R = 1200.

FT.	V.	V/D.	TV.	FT.	V.	V/D.	TV.
79°	99	141·4	99	97°	1	0·1	106
80	3	3·0	102	99·8	3	1·0	109
87	3	0·4	105				

In experiment C, the first fraction contained 94% by volume of alcohol, and thus of the 99 c.c. of alcohol originally taken, 93 c.c. were recovered in the first fraction in one distillation.

In order to afford a comparison between the performance of the rotary column and other standard forms, we have drawn up the following table in which are given data concerning the fractional distillation of 200 c.c. of a mixture of equal parts of benzene and toluene, the distillate being collected at the rate of a drop per second. Under the name of each column is given, corresponding to each fraction, the value of V/D, namely, the volume of the fraction in c.c. divided by its temperature-interval in degrees. The most efficient column is that which gives the highest value to V/D

in the immediate neighbourhood of the boiling points of the pure constituents, and the lowest value elsewhere.

Final Temp. of Fraction.	Hempel Column. 58 cm.	Young 8-section Evaporator Column. 78 cm.	Rotary 7-section Column at 2400 Revs. 32·5 cm.	Young 13-section Evaporator Column. 131 cm.
82°	15·6	25·6	45·0	48·8
84	12·0	15·0	2·3	1·6
86	9·0	4·0	3·0	1·2
88	6·0	2·0	1·5	1·0
100	2·0	2·6	0·5	0·4
108	2·0	0·8	1·2	0·4
110	7·0	3·6	10·0	2·4

As will be seen from the above, the rotary column performed satisfactorily. Another point in its favour is that during the distillation it held a smaller mass of liquid and vapour than any of the other forms.

Owing to the complexity of the factors involved and to our incomplete knowledge of them, it is impossible to give exact directions for determining the real economic efficiency of any type of fractionating column except by direct trials. The best that one can do in the case of a new type is to compare its performance with that of a standard efficient type, paying attention to completeness of separation of the constituents of the mixture with which it has to deal, and to its initial and running costs. No claim is here made that we have established the best form, dimension, or revolution speed for a rotary column, nor, in view of our experience of the diverse behaviours of different mixtures, do we consider that such could be satisfactorily determined except by direct trials with the particular mixture that is to be resolved by distillation into its constituents. However, sufficient evidence has been adduced to demonstrate that the principle of the fractionating column with moving parts introduces a useful innovation, and one that might in certain cases be advantageously adopted in practice. We are at present designing a new model which it is hoped will be more efficient than the one here described.

III.—*The Absorption Spectra of Various Aldehydes and Ketones and some of their Derived Compounds.*

By John Edward Purvis.

The aim of this communication is to discuss the results observed in the following compounds : formaldehyde, paraldehyde, trithio-formaldehyde, α-trithioacetaldehyde, β-trithiobenzaldehyde, α-di-phenylglyoxime, diacetylmonoxime, acetal, methylal, benzylidene-acetone, benzylideneacetophenone, benzylideneacetoxime, benzyl-idenedeoxybenzoin, benzylidenecamphor, cinnamylidenecamphor.

The methods of investigation have been described before. In 1912, the author and McCleland (J., **101**, 1810) and Bielecki and Henri (*Ber.*, **45**, 2819) investigated the absorption bands of various aliphatic aldehydes and ketones. Among these, solutions of form-aldehyde in alcohol and in ether showed no selective absorption.

The following substances exhibit no specific absorption in solu-tion. The concentration of the solution and the name of the solvent are given, and also the positions of the rays from a condensed cadmium spark that were transmitted through varying thicknesses of the solution, increasing by 2 mm. for each photograph (only the first and the last value are given in each case) : *Formaldehyde*, 30% in water; 10 mm., λ 2250; 90 mm., λ 2930. *Paraldehyde*, 2*M* in ethyl alcohol; 12 mm., λ 2150; 90 mm., λ 2560. *Trithio-formaldehyde*, *M*/550 (the highest obtainable) in ethyl alcohol; 20 mm., λ 2560; 60 mm., λ 2680; *M*/5500; 20 mm., λ 2160; 60 mm., λ 2270. *α-Trithioacetaldehyde*, *M*/10 in alcohol; 10 mm., λ 2650; 30 mm., λ 2750; *M*/100; 10 mm., λ 2500; 30 mm., λ 2600; *M*/1000; 10 mm., λ 2180; 30 mm., λ 2350. β-*Trithio-benzaldehyde*, *M*/1350 (the highest obtainable) in alcohol; 20 mm., λ 2570; 60 mm., λ 2750; *M*/13,500; 20 mm., λ 2290; 60 mm., λ 2450. *Methylal*, 2*M* in alcohol; 10 mm., λ 2100; 80 mm., λ 2190. *Acetal*, 2*M* in alcohol; 20 mm., λ 2550; 76 mm., λ 2750; *M*; 10 mm., λ 2450; 62 mm., λ 2570; *M*/10; 10 mm., 2310; 62 mm., λ 2470; *M*/100; 12 mm., λ 2120; 56 mm., λ 2270.

Purvis and McCleland showed (*loc. cit.*) that the vapour of form-aldehyde exhibited a considerable number of narrow bands. Acet-aldehyde has a solution band at 1/λ 3500 (λ 2856), and one large vapour band; chloral has a solution band at 1/λ 3430 (λ 2912), and chloral hydrate has no band, the solution being very transparent to the cadmium rays. To explain these phenomena, it is suggested that formaldehyde unites with the solvent, forming a compound whose formula might be represented as $H \cdot CH(OH)_2$ and is thus comparable with $CCl_3 \cdot CH(OH)_2$. Again, if the formula of paralde-

B*

hyde, which shows no absorption band, is written as (A), it may be suggested that a similar type of condensation occurs with

(A.) $\text{CHMe}<^{\text{O·CHMe}}_{\text{O·CHMe}}>\text{O}$ (B.) $\text{H}_2\text{C}<^{\text{O—CH}_2}_{\text{O—CH}_2}>\text{O}$
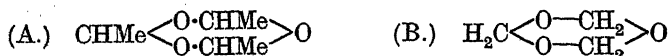
formaldehyde, and its constitution could be described as (B), and this again would explain the absence of specific absorption.

The solution of β-trithiobenzaldehyde showed there was no trace of the two solution bands of benzaldehyde described by Purvis and McCleland (J., 1913, **103**, 1088); and in this respect it is comparable with trithioformaldehyde described above.

The absence of any selective absorption in solutions of methylal and acetal may be explained by a consideration of their constitutional formulæ $\text{H·CH(O·CH}_3)_2$ and $\text{CH}_3\text{·CH(O·C}_2\text{H}_5)_2$. The aldehydic oxygen is fully saturated and there is no centre of vibration to give specific absorption.

α-*Diphenylglyoxime.*—The substance is not very soluble in alcohol, and the strongest solution available was $M/1700$. There appeared to be a very weak band at about λ 2380, corresponding to the very weak band of liquid diphenyl at λ 2300 described by Baly and Tryhorn (J., 1915, **107**, 1058). The following numbers represent some of the observations made between 20 mm. and 60 mm. thickness, increasing by 2 mm. for each exposure.

$M/1700.$	Thickness (mm.) ...	20	60			
	Rays transmitted to	λ 2750	2900			
$M/17,000.$	Thickness (mm.) ...	20	32	40	50	60
	Rays transmitted to	λ 2150	2270	2400 *	2550	2590

The weak band lies between λ 2400—λ 2270 in this solution.

* The stronger Cd lines round about λ 2300 were just visible.

Two solution bands of benzil are described by Baly and Stewart (J., 1906, **89**, 502) at 1/λ 3900 (λ 2563) and 1/λ 2650 (λ 3773), and Hantzsch and Schweite (*Ber.*, 1916, **49**, 213) describe a similar curve. Hantzsch (*Ber.*, 1910, **43**, 1651) found no definite band in *syn*-benzilmonoxime, although the line of absorption is bent a little in the region of 1/λ 2800—1/λ 3250 (λ 3569—λ 3075) and also in the region of 1/λ 4000 (λ 2498). The two benzil bands have completely disappeared in the glyoxime. The author can confirm the absence of selective absorption in diacetyldioxime first noticed by Baly and Stewart (J., 1906, **59**, 502).

Solutions of strengths varying from $M/10$ to $M/10,000$ of diacetyl-monoxime were also examined, but no definite bands were noticed. The general absorption was fairly strong, for through 30 mm. of a $M/10$-solution the rays were absorbed from about λ 3850; through

30 mm. of a $M/100$-solution, from about λ 3370; and through 30 mm. of a $M/1000$, from about λ 2700.

It is clear, therefore, that α-diphenylglyoxime behaves like all oximes in this respect. In this substance, the two CO groups of benzil have been completely eliminated in the oxime, and the specific absorption of the original substance has been destroyed.

Benzylideneacetone.—The author has repeated the observations of Baker (J., 1907, 91, 1490) and Baly and Schaefer (J., 1908, 93, 1808) and confirms the presence of a large band at $1/λ$ 3500 (λ 2856). The author has also repeated the work on the absorption of acetone first described by Stewart and Baly (J., 1906, 89, 492), and of benzaldehyde described by Purvis and McCleland (J., 1913, 103, 1088). The absorption curves of these substances have been drawn (Fig. 1) for comparison with that of benzylideneacetone. The band of the latter substance is narrower than the acetone band, and the two benzaldehyde bands have disappeared.

The vapour of benzylideneacetone was examined in a 200-mm. tube at various temperatures and pressures with the following results :

$T°$.	Pressure in mm.	
50	792	The rays were transmitted to λ 2120.
60	802	The rays were weak between λ 2780 and λ 2420 and then transmitted to about λ 2120.
70	812	The rays were almost completely absorbed between λ 2880 and λ 2400 and then transmitted to λ 2150.
80	822	The rays were completely absorbed between λ 2950 and λ 2350 and then transmitted to λ 2200.
90	832	The rays were absorbed from λ 3000, but the series of Cd lines round about λ 2300 was visible.
100	842	The rays were absorbed from λ 3010, the Cd lines at λ 2300 being very faint.

Similar results were obtained when the vapour was examined at a constant pressure of 757 mm. and at temperatures varying from 40—80°. The radiations of a Welsbach light were used to investigate the more refrangible regions of the visible spectrum. No absorption bands were recorded, and the rays were transmitted to about λ 3200, i.e., as far as the radiation affected the photographic plate. All these experiments prove that the narrow vapour bands of benzaldehyde described by Purvis and McCleland (*loc. cit.*) have disappeared. These authors also proved (*loc. cit.*) that acetone had no narrow vapour bands. The results appear to indicate that the different unsaturated vibratory centres do not act independently of each other. In this direction, the author has pointed out (J., 1914, 105, 2482) that the solution and vapour of benzylidene chloride possess the residues of three benzene solution bands (comparable with the three toluene bands), and that

benzaldoxime has several of these residual bands bordering on a stronger band. The elimination of the oxygen of the CO group in both cases enables the molecule to recover some portion of the vibrations of the original benzene ring.

It was also shown (*loc. cit.*) that cinnamaldehyde had one large band covering the area occupied by the two benzaldehyde bands and that through 30 mm. of a $M/10$-solution the former substance absorbed the rays from λ 3940, *i.e.*, within the areas of the visible spectrum.

Now, in benzylideneacetone the two benzaldehyde bands disappear and the larger single band is not unlike the acetone band. Also through 30 mm. of a $M/10$-solution the substance absorbed the rays from about λ 3850, *i.e.*, within the borders of the visible region. There is no exhibition of any residual benzene bands noted in benzylidene chloride and benzaldoxime. It is apparent, therefore, that the vibrations of the three unsaturated centres of benzylideneacetone do not act independently. Their interacting oscillations produce great absorption and the development of a weak colour.

Cinnamylideneacetone has a large band at about $1/\lambda$ 3200 (λ 3120) according to Baly and Schaefer (J., 1908, **93**, 1808); and at the greatest thickness the line of absorption appears to be at about λ 3815, *i.e.*, at the edge of the more refrangible region of the visible spectrum. This large band is not unlike that of benzylideneacetone.

Benzylideneacetoxime.—Alcoholic solutions of this colourless substance were examined and the curve was drawn (Fig. 1). Comparing this case with benzylideneacetone, it is evident that the colour of the latter depends chiefly on the CO group. In the oxime the line of general absorption and the band are shifted more towards the more refrangible regions. The band is a little wider and less persistent and the substance less transparent in the more refrangible regions. The line of general absorption through 30 mm. of a $M/10$-solution is at λ 3500, and in benzylideneacetone it is at λ 3850.

Benzylidenedeoxybenzoin.—Solutions of this substance were examined and the curve (Fig. 2) shows one very shallow band, the line of general absorption rapidly extending into the visible regions. The line of general absorption through 30 mm. of a $M/100$-solution was at λ 3930. Stobbe and Ebert (*Ber.*, 1911, **44**, 1289) describe a large band in benzylideneacetophenone. The author has repeated the observations and drawn the curve for comparison. The band is wider than that of benzylideneacetone and is shifted more towards the red end.

Cinnamylidenecamphor.—Lowry and Southgate (J., 1910, **97**,

905) describe a solution band of benzylidenecamphor at about
$1/\lambda$ 3450 (λ 2896). The author has repeated these observations,
to compare the phenomena with those exhibited by cinnamylidene-
camphor (Fig. 2). The differences are the greater shift of the
absorption of the latter towards the red, the lessened transparency
of the cinnamylidene compound in the more refrangible regions,
and the wider band. The chief effect seems to be that the additional
unsaturated centre has strengthened the colour and shifted the
band more towards the red. The line of absorption through
30 mm. of $M/10$-solution is at λ 3960 in benzylidenecamphor and at
λ 4250 in cinnamylidenecamphor.

FIG. 1.
Oscillation frequencies.

FIG. 2.
Oscillation frequencies.
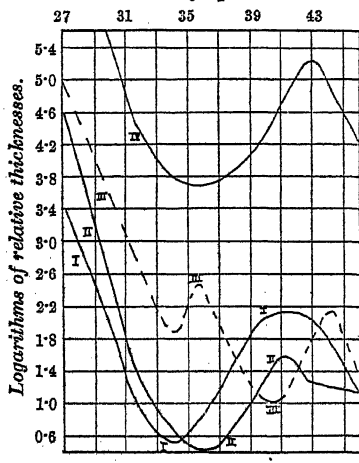
I *Benzylideneacetone;*   II *Benzyl-*
ideneacetoxime;   III   *Benzaldehyde*
(dash); IV *Acetone.*
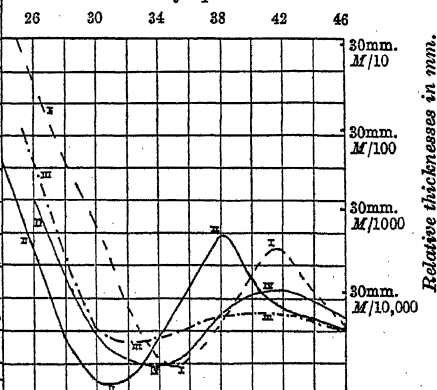
I *Benzylidenecamphor (dash);* II *Cinnamyl-*
idenecamphor; III *Benzylidenedeoxybenzoin*
(dot and dash); IV *Benzylideneacetophenone.*

The outstanding results of these and earlier observations are :
(1) all aldehydes and ketones exhibit selective absorption in well-
defined areas of the ultra-violet region and this disappears when
the aldehydic or ketonic groups are eliminated or neutralised.
Examples of such phenomena are the oximes, paraldehyde, form-
aldehyde, thioaldehydes, methylal, acetal, chloral hydrate. (2) All
other substances which have unsaturated centres also show specific
absorption. These centres may be ethylenic or acetylenic or both,
and may also act in union with other centres such as unsaturated
benzene residues, ketones, and aldehydes. When these oscillatory
centres are successively eliminated the absorption band or bands
are altered in appearance; or the specific bands characteristic of

one or other of the remaining centres are partly developed. There is also a shift of the line of general absorption, and of the remaining band or bands, towards the more refrangible regions. Finally, when all the oscillatory centres are completely saturated, the substance shows no specific absorption and is very transparent. (3) The colour of organic substances, as Dr. Armstrong pointed out long ago, appears to depend largely on the substances possessing at least three unsaturated constituents. Each centre has its own specific influence which is unlike that of the others but with which it acts in co-operation. Substances which have at least three unsaturated centres and are coloured are benzylideneacetone, benzylideneacetophenone, benzylidenedeoxybenzoin, cinnamylidene-acetone, cinnamylideneacetophenone, benzylidenecamphor, cinnam-ylidenecamphor. On the other hand, diacetyl and glyoxal are coloured and they have only two centres. It is suggested that the complete action of the unsaturated centres depends on their chemical type. It can hardly be doubted, for example, that a ketonic or an aldehydic centre exercises more influence in specific absorption than any other.

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IV.—*The Ignition of Gases. Part V. Ignition by Inductance Sparks. Mixtures of the Paraffins with Air.*

By RICHARD VERNON WHEELER.

ONE object of this part of the research on the ignition of gases was to compare the relative ignitibilities of mixtures of methane and air by inductance sparks (low-tension "break-flashes" or momentary arcs) with the values obtained when capacity sparks (high-tension impulsive discharges) were used as described in J., 1920, 117, 903. For, as a source of ignition of gaseous mixtures, an inductance spark (produced when an electric current in an inductive circuit is interrupted by the separation of metallic contacts) differs from a capacity spark mainly in its longer duration, the difference being sufficiently wide to make it of importance to discover whether inductance sparks can be regarded, with capacity sparks, as "momentary" sources of heat (see J., 1924, 125, 1858), or whether they more nearly approach in character "sustained" sources, such as heated surfaces (see *ibid.*, p. 1869).

The character of inductance sparks is most susceptible to changes

in the conditions under which they are produced, so that consider-
able variation can exist in their incendivity. Fig. 1, constructed
mainly from oscillograph records, represents the variations, with
time, of current, resistance, voltage and total heat generated in
an inductance spark-gap produced by the rapid separation of metallic
contacts. As the area of contact, anterior to rupture of the circuit,
decreases, the electric resistance at that point increases and heat
is generated. Eventually, the last remaining points of contact
become so hot that the metal volatilises and, at the actual moment
of break of circuit, a conducting band of metallic vapour is pro-
duced. This band rapidly increases in length as the fracture is
widened, until the spark can no longer be maintained. With a
spark of this general character, just capable of igniting a given
inflammable mixture, ignition most
probably occurs towards the end of its
duration, but the precise moment
depends upon the exact character of
the spark as determined by the rate
of increase of resistance and of decay
of current in it. For these reasons,
in any attempt, such as is made in
this research, to determine the relative
ignitibilities of different gaseous mix-
tures by means of inductance sparks
of different intensities, we must recog-
nise not only the changes, measured
or deduced, purposely made in the
intensity, but also the changes in the
character of the sparks. These changes
in character may be either inadvertent (as when the condition of
the metallic surfaces that are separated changes) or a necessary
concomitant of a change in intensity (as when the inductance of
the circuit is purposely altered).

FIG. 1.

    In the production of inductance sparks there are six chief vari-
ables, which can be divided into two groups according as they relate
to (a) electrical or (b) mechanical conditions. In the former class
are : (1) The self-inductance of the circuit; (2) the impressed voltage;
and (3) the current flowing in the circuit before rupture. The latter
class includes : (4) The nature of the metal at the spark gap;
(5) the rate of break of circuit; and (6) the area of contact at the
moment of break. Each of these variables can be more or less
effectively controlled independently and the influence of each can
therefore be determined. The most difficult to control and of
which to gauge the influence is the last-named, and most of the
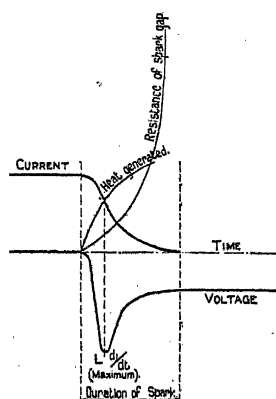
experimental difficulty of this work has been in maintaining constancy of this factor. For with the production of a spark there is a change in the condition of the surfaces at which it passes and with a readily oxidisable metal the change may be sufficient to alter considerably the area of contact available for successive sparks, as was observed when the influence of different metals at the spark gap was studied. Platinum or gold surfaces were found to be least susceptible to change and the former have been used for the majority of the experiments. Three different types of apparatus, each of which had its advantages for particular series of experiments, have been used. These are described in the experimental portion of this paper and are referred to as A, B and C.

Electrical Conditions.

With an inductive circuit carrying continuous current, the energy that should, theoretically, appear in the break-flash is the amount of energy stored electromagnetically in the system and should therefore amount to $\frac{1}{2}Li^2$. This expression does not, however, take into account losses in the circuit or absorption at the sparking-points, and although it might be permissible to express the relative incendivities of sparks produced under constant circuit conditions (with a given apparatus) by their energy values, it would be misleading to suggest a comparison of these values with others obtained under different circuit conditions and with a different apparatus for producing the sparks. The relative ignitibilities of different gaseous mixtures are therefore expressed in this paper simply by the values of the currents (in amperes) flowing in the circuit at the moment of interruption which yielded an inductance-spark just capable of causing ignition.

(1) *The Inductance of the Circuit.*—A number of inductances of known magnitudes were prepared, consisting of coils of silk-covered copper wire wound on cores of wood so as to be of constant value at all currents. These were introduced into the circuit from a battery of dry cells and the current at 90, 60, and 30 volts required for the ignition of different mixtures of methane and air by a break-flash at platinum contacts was determined, using apparatus A, which enabled a rapid break of circuit to be obtained. A number of the results are shown graphically in Fig. 2, in which percentages of methane are plotted against igniting-currents, each curve being for a given value of inductance and impressed voltage of the circuit. From the values used in the construction of these curves, the relationship between the igniting current for a given mixture and the inductance of the circuit can be determined. Thus Fig. 3 shows the relationship when mixtures containing 6·0, 7·0, and 8·0% of methane

were used and the impressed voltage was 90; additional values used for these curves are the igniting-currents when the inductance was 0·00815 henry, namely 1·52, 1·18, and 0·94 amp. for the 6·0, 7·0, and 8·0% mixtures, respectively. The relationship, between the values of L of 0·008 and 0·095 henry, can be expressed by the equation $Li^{1·4} = k$; that is to say, the energy required in the circuit before break ($\frac{1}{2}Li^2$) to produce the igniting sparks was nearly constant. This result is deceptive, however, for in other series of experiments, carried out with a different method of producing the sparks, the value $\frac{1}{2}Li^2$ was by no means constant. (In this con-
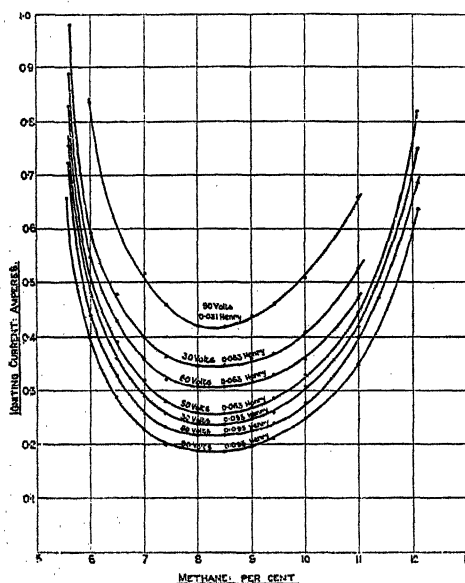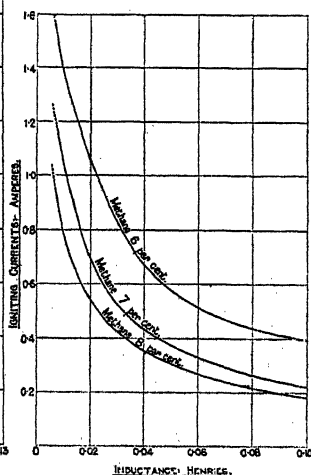
FIG. 2.   FIG. 3.

nexion, see Morgan, J., 1919, **115**, 24). A simple law connecting i with L in ignition experiments could only be expected if sparks of the same character could be produced with different values of L, and it would appear not to be possible to vary the intensity of a spark (by varying the inductance) without altering its character; for at any particular instant during a break-flash, when L is the inductance of the circuit, r the resistance of the spark-gap, R the resistance of the rest of the circuit, and V the impressed voltage, the value for the current is $(V - Ldi/dt)/(r + R)$, whilst its limiting value at the outset is V/R.

(2) *The Impressed Voltage.*—In general, it can be stated that the amount of current in the circuit is of far greater importance than

the impressed voltage as regards the igniting power of the flash produced on breaking the circuit. Especially is this so with highly self-inductive circuits. Thus an 8·0% methane–air mixture was ignited by the break-flash with a current of from 0·24 to 0·25 ampere under the conditions of the experiments at any voltage between 10 and 30, the self-induction of the circuit being 0·095 henry. With higher circuit voltages, however, the igniting current decreases, as the results recorded in Fig. 2 show. When the contacts at which the break-flash is produced are together, the voltage drop between them is zero; as soon as they are completely separated, the voltage between them is equal to the impressed voltage. During the separation of the contacts two actions are tending to make the arc between them persist, namely, the induced voltage, which progressively diminishes, and the impressed voltage, which progressively increases. If the impressed voltage is high, it will contribute materially to the maintenance of the arc. This effect is more marked when the rate of separation of the contacts is comparatively slow, so that the value of the induced voltage (Ldi/dt) is low. For example, a series of experiments using apparatus B, in which massive electrodes of platinum are drawn apart slowly, gave the results shown in Table I.

TABLE I.

Ignition of a 7·8% Methane–Air Mixture. Inductance of Circuit 0·095 henry.

E.M.F. (volts)	25	40	60	70	80	90	110	140
Igniting current (amps.)	1·18	1·00	0·80	0·73	0·66	0·60	0·50	0·38

It is evident that the energy of the sparks, as deduced from the expression $\frac{1}{2}Li^2$, does not give a true measure of their incendivity; as is also apparent from the fact that the igniting currents for the same mixture of methane and air (7·8%) as determined in the two apparatus A and B, with the same circuit conditions before break (e.g., voltage 90 and inductance 0·095 henry) is markedly different.

(3) *The Current.*—We have to consider the effect of using alternating instead of continuous current. Thornton, in his researches on the ignition of gaseous mixtures by inductance sparks (*Proc. Roy. Soc.*, 1914, **90**, *A*, 272), has employed alternating currents at various frequencies and voltages, and, so far as the ignition of mixtures of methane and air is concerned, has recorded that much larger currents are required to produce ignition than with direct current. For example, under the conditions of his experiments, the igniting current for a 9·5% methane–air mixture was 0·5 ampere with continuous current at 200 volts (inductance of circuit not stated),

whilst with alternating current at 200 volts and 100 periods per second it was 20 amperes root-mean-square (r.m.s.) value (or 28 amperes crest value), although the arrangement of the resistance and inductance of the circuit is stated to have been the same as that used for the experiments with continuous currents. Similar wide differences with alternating current at lower voltages and frequencies are recorded by Thornton.

To check this remarkable result, duplicate series of experiments were made with apparatus A, using (a) continuous current at 35 volts with 0·095 henry inductance and (b) alternating current at 25 volts r.m.s. value (35·3 volts crest value) with 0·098 henry inductance, 50 periods per second. The break-flashes were produced between contacts of platinum. In the experiments with alternating current, the procedure was to produce a series of 50 sparks (with a given current) at 5 seconds' interval in a charge of the mixture of methane and air undergoing test. If no ignition occurred, a fresh charge of mixture was admitted to the explosion vessel and a further 50 sparks were passed with the current value increased by 0·01 ampere. This process was repeated until ignition occurred, when the current value was reduced by 0·01 ampere and two or three hundred sparks were passed in several charges of the mixture to ensure that the least igniting current had been determined. The reason for this procedure, which was unnecessary with continuous current (although it was followed in several of the trials in order to make the comparison exact), was that it was impossible to arrange that the break-flash should be produced always when the current was at the crest of its cycle. Ignition was, in fact, more " difficult " with alternating current, because the production of a spark at the crest value of the current was a matter of chance. The lowest current at which ignition could be obtained was not, however, much different from that required when continuous current was used. Typical results are recorded in Table II.

TABLE II.

Ignition of Methane–Air Mixtures using (a) *Continuous and* (b) *Alternating Current* (50 ⁓). *Voltage* 35. *Inductance* 0·095 *henry.*

Methane %	6·15	7·10	7·60	8·00	8·50	9·00	9·60	10·20	10·90
Igniting current (amps.). Continuous	0·43	0·30	0·26	0·24	0·24	0·25	0·28	0·32	0·42
Alternating (crest values)	0·49	0·36	0·30	0·26	0·24	0·25	0·26	0·30	0·44

It was anticipated that, under certain conditions, rather more current would be required in the break-flash to ignite a given

mixture when the source of supply was alternating than when it was continuous, for the reason that the rapidly changing value of the former might shorten appreciably the duration of the transient arc, and the fact that the values for the igniting currents of the mixtures containing the lower percentages of methane are rather higher with alternating than with continuous current is probably due to this effect.

Mechanical Conditions.

(4) *The Nature of the Metal at the Spark-gap.*—Since an inductance spark is of the nature of a transient arc, current being conducted across the gap through the vapour of the metal, it would seem probable that the lower the volatility of the metal conductor the lower would be the igniting current for a given mixture, other conditions being constant, for less energy would be expended in forming a path for the current, or that path might remain open during a longer interval of time.

Several series of experiments to determine this question were made using apparatus C, which was designed to allow of the ready interchange of contacts of different metals whilst preserving as nearly as possible all other experimental conditions constant. The results are summarised in Table III. Mixtures of methane and air containing between 8·35 and 8·55% of methane were used and the inductance of the circuit was 0·03175 henry.

TABLE III.

Igniting Currents with Contacts of Different Metals. (Mixtures of Methane and Air).

Metal.	Boiling point.	Igniting current. Ampere.			Second series.
		First series.			
		At 80 volts.	At 100 volts.	At 120 volts.	At 120 volts.
Cadmium	778°	—	—	0·22	0·23
Zinc	918	0·34	0·26	0·23	0·25
Aluminium	1800	—	—	—	0·30
Silver	1955	0·44	0·41	0·38	0·32
Tin	2270	0·66	0·53	0·45	—
Copper	2310	—	—	0·49	0·38
Nickel	2330 ?	0·63	0·58	0·55	0·39
Iron	2450	0·58	0·52	0·49	0·42
Platinum	2450 ?	0·65	0·56	0·48	0·48
Gold	2530	0·86	0·59	0·50	0·34

The determinations presented considerable difficulty, for not only was it necessary to ensure that the area of contact between the poles at the moment of separation was the same in parallel experiments with different metals (a matter requiring fine adjustment of the apparatus), but with all the metals except platinum

and gold the production of a single spark sufficed to oxidise the surfaces to a greater or less degree (thus altering the area of metallic contact) so that in most instances it was necessary to repolish the surfaces between each break-flash.

In Table III the metals have been arranged in order of their boiling points (as recorded in Kaye and Laby's "Physical and Chemical Constants," 1921) and it is clear that there is a close relationship between those values and the "igniting currents," under standard electrical conditions, of a given mixture of methane and air. The energy available at break is utilised mainly in producing an arc of volatilised metal, and a given quantity of energy presumably produces an arc of short duration if the metal has a high boiling point and an arc of longer duration when the boiling point is relatively low. The duration of the break-flashes with the metals that gave the highest and the lowest results for the igniting currents (gold, platinum, zinc, and cadmium) were determined by photographing them on a rapidly revolving plate. The results are recorded in Table IV.

TABLE IV.

Duration of Break-flashes that Causes Ignition of an 8·5% *Methane–Air Mixture.*

Metal.	Relative Igniting-current at 120 volts. Ampere.	Duration of Break-flash. Second.
Cadmium	0·23	0·00321
Zinc	0·25	0·00234
Platinum	0·48	0·00081
Gold	0·50	0·00070

Thus, under standard conditions, a break-flash between cadmium surfaces with a current of 0·23 ampere flowing in the circuit before interruption lasts four times as long as one between platinum surfaces with a current of 0·48 ampere, a fact which no doubt accounts mainly, if not entirely, for both sparks having the same incendivity although the amounts of energy in the circuit at their moments of formation are so different.

In this connexion, reference may be made to determinations by v. Lang (*Wied. Ann.*, 1887, **31**, 384) of the minimum arcing potential, using poles of different metals, for although his results refer to maintained arcs, which the break-flashes are not, they give a measure of the degree of ease with which such arcs can be produced. The values depended essentially upon the distance apart of the poles and the current flowing in the circuit, and could be expressed by a formula $p = a + bli$; in which p is the observed *P.D.* in volts between the poles, l is the distance apart of the poles in mm., and i is the current in amperes, b being a constant (independent of the

current) and a the *E.M.F.* required to maintain the arc. Taking the somewhat arbitrary values of 0·5 ampere for i and 0·5 mm. for l, as lying within the range of the experiments recorded in Table III, v. Lang's determinations were : Cadmium, 10·9; zinc, 20·0; silver, 20·0; copper, 24·0; iron, 25·2; nickel, 26·4, and platinum, 27·8 volts, showing that the ease with which the arc is maintained is directly connected with the volatility of the metal.

(5) *The Rate of Break of Circuit.*—Since the incendivity of the break-flashes depends in part on the inductance voltage and since the magnitude of the inductance voltage depends on the product of the coefficient of self-induction L and the rate of change di/dt of the current in the circuit, it follows that the rate of break of the circuit—the speed at which the metallic contacts are separated—affects the incendivity of break-flashes produced under otherwise identical conditions. This is demonstrated qualitatively by experiments made with apparatus C, using platinum electrodes, which showed that the igniting-current for a given mixture of methane and air was 0·24 ampere when the rate of break was "rapid" and 0·60 ampere when it was "slow," other conditions remaining constant.

(6) *The Area of Contact at the Moment of Break.*—Since the production of a break-flash depends essentially on the temporary provision of a path for the current through a band of metallic vapour, it follows that the incendivity of a spark produced under otherwise identical conditions will be affected by changes in the area of metallic contact at the moment of break; for the smaller the area of contact at the instant of rupture the more readily will the mass of metal that then remains to form a conductor be turned into vapour that can continue the conduction, and the smaller the volume of vapour thus produced the greater will be the amount of energy concentrated in it and the greater, in consequence, will be its incendivity. Experiments (made with apparatus C) using pole pieces, of platinum, of different cross-sectional area with their surfaces carefully polished and aligned showed that a lower igniting-current was required for a given mixture of methane and air (under otherwise identical electrical conditions) the smaller the area of the poles.

Further information on the effect of the area of contact at the moment of break was obtained when the poles were made of a readily oxidisable metal, such as zinc, for then, unless the surfaces were repolished between each spark, the igniting current regularly decreased to a minimum (at which sparking ceased) as oxidation proceeded; presumably because the coating of oxide gradually reduced the area of metallic contact.

From the fact that so many factors, each having considerable influence on the character of the sparks, have to be taken into account, it will be realised that repetition of the results of apparently parallel experiments was by no means easy to obtain. No success attended experiments in which the break of circuit at which the flash occurred was made by hand; it was only by rendering all possible operations mechanical and automatic that any degree of consistency in the igniting currents could be secured, and during the course of each series of experiments repeated checks had to be carried out with a standard mixture (8·5% of methane in air) under standard conditions to ensure that no unnoticed change had taken place in the condition of the contacts.

From this study of the electrical and mechanical conditions necessary to produce inductance sparks of uniform character, it appeared that the optimum conditions were obtained if : (*a*) The battery voltage was low and the inductance fairly high, so as to ensure that the sparks should be maintained primarily by the inductance voltage; (*b*) the metal contacts at which the sparks were formed were not readily oxidised; (*c*) the rate of separation of the contacts was rapid; and (*d*) the area of contact at the moment of break was small. Comparative series of experiments were made with mixtures of each of the paraffins, methane, ethane, propane, butane, and pentane, with air, using continuous current at 30 volts with 0·095 henry inductance. The sparks were formed between contacts of platinum in apparatus A, which was judged to provide the optimum mechanical conditions for the production of sparks of uniform character.

The curves relating percentage of inflammable gas in the mixtures with air to " igniting-currents " were similar, with each hydrocarbon, to those obtained when secondary discharges (capacity sparks) were used as the means of ignition (see J., 1924, **125**, 1860) save that, in each instance, differentiation between the more readily ignitible mixtures was not so marked. The same differences in the degree of ignitibility of the paraffins was also observed, but again the differences were not so marked. The essential data are given in Table V.

The general result of these experiments is to show that, so far as the paraffin hydrocarbons are concerned, inductance sparks can be considered similar in effect to capacity sparks as means of ignition, despite the wide difference there is in the two types both as regards duration and volume. The longer duration and larger volume of the inductance sparks apparently have the effect of masking small differences in the ignitibility of those mixtures that are most readily ignited.

TABLE V.

Mixtures of the Paraffins with Air.

Combustible gas.	Mixtures most readily ignited by secondary discharge.	Relative igniting currents. Secondary discharge.	Mixtures most readily ignited by inductance sparks.		Relative igniting currents. Inductance sparks.
	(J., 1924, **125**, 1863.) Per cent.	Ampere.*	Range. Per cent.	Mean.	Ampere.
Methane	8·3	0·59	7·8—9·0	8·4	0·24
Ethane	6·7	0·47	6·0—6·8	6·4	0·15
n-Propane	5·1	0·36	4·8—5·4	5·1	0·12
n-Butane	4·2	0·48	3·8—4·4	4·1	0·15
n-Pentane	4·0	0·52	3·6—4·2	3·9	0·23

* Currents in the primary circuit (see J., 1920, **117**, 903.)

EXPERIMENTAL.

Apparatus A (Fig. 4). A brass rod passing through the side of a spherical glass vessel of 100 c.c. capacity carried at its end a pointed strip of platinum, A, to form one of the electrical contacts at which the inductance spark should be produced. The other contact was a platinum rod, B. This rod was mounted on a glass support which passed through the ground-glass bearing, C, and could be caused to revolve by means of the pulley, D, driven by an electric motor. The glass support was hollow so as to enable electrical connexion to be established (by means of a copper wire, *E*, passing through it) between short pieces of thick platinum wire fused into either end. The upper platinum wire carried the contact rod, B, and the lower wire dipped into a mercury-cup, F, whence the electric circuit could be completed. The rod was revolved at such a speed as to make contact every 5 seconds with the strip, which was bent at an angle (in a manner not apparent from Fig. 4) so that the rod as it revolved remained in contact with it during about half a second and then released it suddenly, forming a quick break of circuit.

Apparatus B (Fig. 5).—The poles were cones of platinum fused into hollow glass supports which passed through ground glass bearings on opposite sides of a glass globe of 100 c.c. capacity. One support, A, was held by light springs (which allowed it a small amount of movement) so that the platinum pole was normally at the centre of the globe. The support, B, was attached to a strong spring, C, which could pull it half-way through the bearing. A revolving cam (not shown in the diagram), acting on the rod, D, pushed this support against the pull of the spring so that its platinum pole made contact periodically with that of A. Electrical connexions were made through copper wires passing within the hollow

supports as in apparatus A. The cam was revolved by an electric motor at such a speed that contact between the poles was made and broken every five seconds and the arrangement was such that contact was maintained during half a second.

Apparatus C (Fig. 6).—This apparatus was similar in design to one used by Thornton (*The Electrician*, Sept. 8th, 1916). A small solenoid, A, was supported within a cylindrical explosion vessel of glass of 100 c.c. capacity. Its plunger carried one of the poles, a rod 0·5 mm. in diameter. The other pole, 1·5 mm. in diameter, was carried on a fixed support, B. The pole pieces were

FIG. 4.
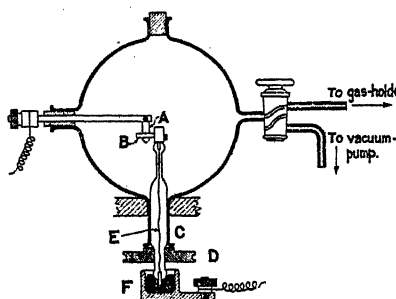
FIG. 6.
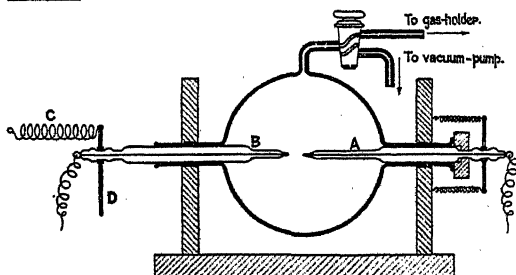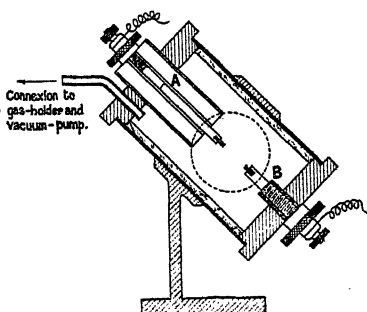
FIG. 5.

removable so that different metals could be used. When the solenoid was out of action, its plunger dropped so that the end surface of the pole attached to it rested on that of the fixed pole, but on passing an electric current through the coils the plunger was rapidly withdrawn so that a quick break of circuit occurred at the surfaces of the poles. Make and break of electric circuit in the solenoid (the electrical connexions to which are not shown in the diagram) were made automatically so that the poles were separated every five seconds.

Each apparatus could be evacuated so as to enable gaseous mixtures of known composition to be introduced. The mixtures

were stored in glass gas-holders over glycerol and water and were analysed before use. In each series of experiments, the electric circuit included a Post Office resistance box (the coils of which were non-inductively wound) to enable small changes of current to be made, a measured inductance and an ammeter, which was short-circuited when the break-flashes were produced. Except during the experiments with alternating current, the source of supply was a battery of dry cells.

These experiments were carried out during the years 1914 to 1916. I was assisted throughout by Mr. W. Mason, whilst the determinations of the duration of break-flashes with different metals were made by Mr. W. Shepherd, to both of whom I am greatly indebted.

EXPERIMENTAL STATION,
        ESKMEALS, CUMBERLAND.   [*Received, November 3rd*, 1924.]

V.—*The Partial Formaldehyde Vapour Pressures of Aqueous Solutions of Formaldehyde.   Part I.*

By ETHELBERT WILLIAM BLAIR and WILFRID LEDBURY.

A LARGE number of processes, based on methods of controlled oxidation of various hydrocarbons (Glock, D.R.-P. 109,014, 1898; Walters, F.P. 168,785; Willstätter and Bommer, *Annalen*, 1921, 422, 36; Blair and Wheeler, *J. Soc. Chem. Ind.*, 1922, 304T; 1923, 81T; Berl and Fischer, *Z. angew. Chem.*, 1923, 36, 297; Johnson, B.P. 199,885, 1922) have been proposed, from time to time, for the production, on a commercial scale, of aqueous solutions of formaldehyde. The comparatively low concentration of formaldehyde vapour in the effluent gases from such oxidation processes may easily result in depreciated yields of the required product, on account of low absorption efficiencies. It is the object of the present investigation to determine the partial formaldehyde vapour pressures of aqueous formaldehyde solutions of different strengths, and hence to ascertain whether, under equilibrium conditions of absorption, it is possible to effect, more or less completely, the fixation of highly diluted vapours of formaldehyde. Blair and Wheeler (*loc. cit.*) have shown that, under carefully regulated conditions, the slow oxidation of ethylene yields dilute formaldehyde vapours of concentration of the order of 1·0 to 2·0 mg. per litre, corresponding to vapour pressures of about 0·5 to 1·0 mm. of mercury respectively. The investigations carried out by the same authors, with the object of producing formaldehyde by the controlled oxida-

tion of methane, showed that formaldehyde vapours, ranging in concentration from 0·2 to 3·0 mg. per litre, corresponding to partial pressures of 0·13 to 1·65 mm. of mercury, were obtainable under the conditions of their laboratory experiments. In this connexion, it is of importance to determine the maximum strengths of aqueous formaldehyde solutions which are obtainable by the continuous absorption of such vapours under specified conditions. By a study of the partial formaldehyde vapour tensions of solutions at 0°, and by a comparison of the values so obtained with the corresponding values for 20°, the merits or demerits of low-temperature condensation, from the point of view of formaldehyde fixation, can be established. Further, the data derived at the lower temperature should indicate the feasibility, or otherwise, of obtaining formalin solutions of moderate strengths, by processes of chilling moist air or other gas containing small concentrations of the vapour.

EXPERIMENTAL.

Treatment of Formalin Solutions.—Samples of formalin, of approximately 40% strength by volume, and obtained from various sources, were found on analysis to contain varying amounts of methyl alcohol as impurity. The formaldehyde present was estimated by the hypoiodite method of Romijn (*Analyst*, 1897, **22**, 221; see also *Chem. Ztg.*, 1901, **25**, 740; *Ber.*, 1898, **31**, 1979; 1901, **34**, 2817), which, for sufficiently diluted solutions, provides trustworthy data, even when methyl alcohol is present (Bergstrom, *J. Amer. Chem. Soc.*, 1923, **45**, 2150). From a determination of the total carbon content in a given weight of formalin (Blank and Finkenbeiner, *Ber.*, 1906, **39**, 1326), it was possible to arrive at the quantity of methyl alcohol present in the solution. In particular cases, methyl alcohol was present to the extent of 5·0 to 10·0% by weight. It has been suggested by Ormandy and Craven in their " Note on Aqueous Formaldehyde Solutions," read before the Chemical Society, that the discrepancies in the previously published values for the densities of such solutions arise from the presence of methyl alcohol, and their results appear to substantiate this contention. In studying the physical properties of aqueous formaldehyde solutions, it is therefore imperative that any contaminating methyl alcohol should be eliminated. These workers succeeded in removing methyl alcohol from formalin solutions by prolonged refluxing with water; they showed that both the refractive index and the density of a purified formalin solution are linear functions of its concentration. Their data are in agreement with those obtained as a result of a similar investigation by Auerbach and Barschall, who, however, prepared aqueous solutions by passing nitrogen over heated paraformaldehyde

and absorbing in distilled water the formaldehyde vapour carried forward. The removal of methyl alcohol was effected, in the present instance, by refluxing the solutions with distilled water, the proportion of the latter being determined by the strength of the formaldehyde solution required. For this purpose was employed a litre flask, to which was attached a tube, 1 inch in diameter and 28 inches in length, packed to within a few inches of the top with glass beads. The heating was regulated so that the temperature registered at the head of the column was approximately the boiling point of methyl alcohol (66°). Refluxing for a period of about 36 hours sufficed to remove methyl alcohol from 500 c.c. of the solution ; the odour of the alcohol, however, could not be detected when the refluxing had proceeded for only a few hours. Acetone was absent from the solution after refluxing. Incidentally, it is of interest in this connexion to note that the above method for the removal of methyl alcohol forms the basis of a recent patent for obtaining formalin with only a low content of methyl alcohol (Hirchberg, B.P. 199,759, 1922). The elimination of methyl alcohol from formaldehyde solutions, having concentrations of approximately 40% by volume, had a marked effect on the stability of these solutions, the tendency for paraformaldehyde to separate being enhanced by the removal of the alcohol. Thus a solution containing 5% of methyl alcohol and having a formaldehyde content of 41·0 g. per 100 c.c. did not deposit paraformaldehyde on prolonged exposure at 0°, whilst with an uncontaminated solution, containing 38·7 g. of formaldehyde per 100 c.c., a similar exposure caused the development of an opalescence within a few hours, and the eventual deposition of the solid white polymeride. This observation is not, however, in agreement with a surmise put forward by Hirchberg (*loc. cit.*), to the effect that methyl alcohol promotes the production of acetals such as methylal, which are stated to be conducive to the polymerisation of formaldehyde. In consequence of the separation of paraformaldehyde at 0° from the more concentrated formaldehyde solutions freed from methyl alcohol, it was not possible to determine the partial formaldehyde vapour pressures at 0° of solutions having strengths appreciably greater than 30%.

Subsequent to analysis, the formaldehyde solutions, obtained as a result of the above treatment, were allowed to stand at 15° over a prolonged period before being used for the vapour pressure measurements at 20° or 0°. To ascertain the effect of the presence of small amounts of methyl alcohol on the partial formaldehyde vapour pressures of the solutions, the pure alcohol was added to a series of the latter in such amounts as to provide in each case a constant ratio, CH_4O/CH_2O.

Method of Determination.—On account of the comparatively low vapour pressures involved at the ordinary temperature and more especially at 0°, even in the case of solutions approaching the strength of 40% by volume, the "dynamic" or "flow" method was employed in these determinations. Each "carburettor" was charged with 75 c.c. of the formaldehyde solution under investigation, this, in the case of a 40% formaldehyde solution, corresponding to the presence of 30,000 mg. of formaldehyde. At 20°, the passage of 100 litres of moist air through this solution, at the rate of 1·0 litre in 30 mins., effected the removal of only about 250 mg. of formaldehyde, so that for the purpose of computing formaldehyde vapour pressures the concentrations of the formalin solutions were assumed to remain constant during a run involving, say, the passage of 5, 10, 20, or 40 litres of moist air. At 0°, it was possible to pass through the solution much larger volumes of moist air without appreciably affecting the concentration. The estimation of the formaldehyde, carried over by the air stream into the absorption worms, was made by using the hypoiodite method of Romijn (*loc. cit.*), and from the data thus obtained the partial vapour pressure of the formaldehyde was calculated by use of the formula of Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309) :

$$P = 760v_2/(v_1 + v_2) \text{ mm. of Hg,}$$

where $v_2 = 22·4 \ W/M$ litres, is the volume occupied by the formaldehyde vapour alone and M its molecular weight, whilst v_1, the volume of the air used, reduced to *N.T.P.*, is given by the expression

$$v_1 = 273Vp/760(273 + t).$$

V is the unreduced volume of the air, p the pressure of the air collected in the final gas-holder, after necessary corrections have been made for water-vapour tension, and t is the temperature of the air collected in the gas-holder. An account of the applications and limitations of the "dynamic" method of determining vapour pressures is given by Thomas and Ramsay (J., 1923, **123**, 3257), who cite the views of Perman (*Proc. Roy. Soc.*, 1904, **72**, 72; *J. Physical Chem.*, 1905, **9**, 96), the latter, after a careful investigation of the subject, having concluded that, provided proper precautions are taken, the method is capable of yielding sufficiently accurate results.

Apparatus.

The accompanying diagram (Fig. 1) shows the details of the apparatus employed in this investigation. A controlled supply of compressed air was passed through a dust-filter, A, consisting of an enclosed plug of glass wool, and after travelling beyond the stop-cock B, and the pressure regulator, C, was bubbled successively through potash solution and distilled water in D and E, respectively.

A calibrated differential rate-gauge, constructed on the Venturi principle, served to indicate the velocity of the air, which was regulated by means of the stop-cock, B.   Following the differential rate-gauge was a water manometer, G, whch gave the pressure of the air before its passage through the " carburettor " or " carburettors " and the subsequent Winkler worms.   With the exception of the final gas-holder, the remainder of the apparatus, following the water manometer, was immersed in a water thermostat.   The bath was

Fig. 1.
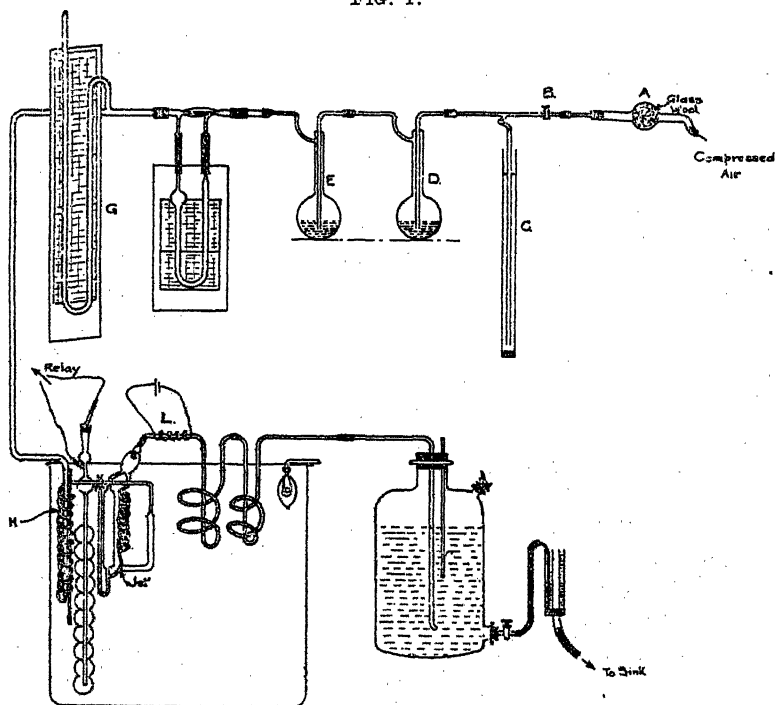
inserted in a large wooden box, and the intervening space between the bath and the walls of the box was loosely packed with lagging, consisting of a mixture of magnesite and asbestos fibre. For the experiments at 20°, the requisite temperature was maintained (within ± 0·05°) by means of a Lowry thermo-regulator, whilst ice uncontaminated with foreign substances was introduced into the bath to keep the temperature at 0°.   The long worm, H, served to bring the inflowing air to the required temperature.   This was followed by a specially designed " carburettor " (or, in the experiments at 0°, by two " carburettors ") containing 75 c.c. of the formaldehyde solution under investigation.   The object of its

construction was to permit the incoming stream of air to pass through the formaldehyde solution in the vertical worm, and to cause the air bubbles, as they emerged into the splash-trap at the top, to force over a part of the formaldehyde solution at the head of the worm into the glass reservoir shown. Fresh formaldehyde solution was thus drawn in at the base of the vertical worm and the unsaturated air came at the outset into contact with fresh formalin solution. At 20°, when two such "carburettors" were connected in series, the amount of formaldehyde vapour carried over by a given volume of air was practically unchanged; hence, at 20°, one "carburettor" only was in use during the greater part of the investigation. The air, saturated at this stage with formaldehyde vapour, passed along the horizontal tube, L, which, in the experiments at the higher temperature, was maintained above the temperature of the bath by an electrically heated coil of resistance wire. Under these conditions, no condensation of water vapour and consequent premature absorption of formaldehyde vapour occurred during the passage of the vapour-laden air along the tube. For the absorption of formaldehyde vapour, two or three Winkler worms containing distilled water were connected in series. The issuing air, stripped of formaldehyde vapour, entered a graduated, water-filled gas-holder at a pressure which was maintained constant, throughout the whole of the experiments, by means of a constant-level overflow. By employing a constant height of formaldehyde solution in the "carburettor" and constant heights of water in the Winkler worms, and by making the necessary alterations in the level of the overflow, the pressure of the air entering the "carburettor," and issuing therefrom, was kept constant. Thus the pressure conditions throughout the whole series of determinations were standardised. Such an adjustment of pressure conditions is necessary, since the amount of formaldehyde carried over by a given reduced volume of air is dependent on the pressure of its delivery as well as on the temperature. The air was forced through the apparatus at a velocity of 1 litre in 30 mins., since it was found from preliminary trials that if the rate of flow was diminished below this value, the amount of formaldehyde vapour per unit volume of air was unaltered for a given formalin solution. Adopting the method of procedure outlined above, a number of determinations were made of the partial formaldehyde vapour pressure of each solution under investigation. For each determination, totals of 5, 10, 15, or 20 litres of moist air were passed, according to the strength of the formalin solution in the "carburettor."

As a result of data derived from earlier experiments, it was found justifiable to dispense with the third Winkler worm of the absorption

train, since even in the case of the relatively concentrated vapours, issuing from a solution containing 38 g. of formaldehyde per 100 c.c., there was no detectable amount of formaldehyde in the water at this stage. In the case of the second absorption worm, small amounts of formaldehyde of the order of 0·1 to 0·2 mg. were found condensed during the passage of the more concentrated vapours. This worm was permanently retained throughout the investigation.

Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions at 20°.

Formalin solutions, from which methyl alcohol had been eliminated in the manner previously described, were exposed at 15° before

Fig. 2.

Litres of air passed through formaldehyde solutions.
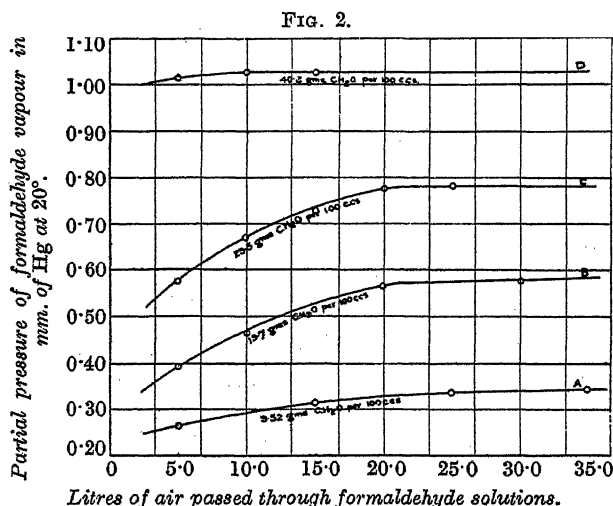
introduction into the " carburettor." The " carburettor " and its contents were then left over-night in the thermostat at 20°, prior to the vapour-pressure determinations.

With the exception of the formaldehyde solution of approximately 40% strength, all the solutions examined exhibited exceptionally low initial formaldehyde vapour pressures, but, as increasing volumes of air, for successive determinations, were passed through each of these solutions, the pressure values increased, rapidly at first, then more slowly, rising to constant maximum values.

The accompanying curves, A, B, C, and D (Fig. 2) depict graphically the relationship between the partial pressure of the formaldehyde vapour in mm. of mercury and the total volume of air in litres passed through a solution of given strength. The examination of the formalin solution containing 40·2 g. of formal-

dehyde per 100 c.c. did not reveal, on the part of the partial pressure, any marked tendency to increase in magnitude, such as was evidenced with the more dilute solutions.

The equilibrium or asymptotic values of the formaldehyde vapour pressures, that is, the constant values reached when the passage of a sufficient volume of air through the solutions had brought about apparent equilibrium conditions between the liquid and vapour phases, are given in Table I, together with the corresponding concentrations of formaldehyde vapour in the effluent air.

<div align="center">TABLE I.</div>

Gms. of formaldehyde per 100 c.c. of formalin solution	9·52	19·7	29·5	31·1	40·2
Mg. of formaldehyde vapour per litre of issuing air	0·59	1·01	1·39	1·40	1·75
Partial pressure of formaldehyde vapour in mm. of mercury	0·340	0·575	0·780	0·795	1·025

FIG. 3.   FIG. 5.

Gms. of formaldehyde per 100 *c.c. of solution.*   *Gms. of formaldehyde per* 100 *c.c. of solution.* $CH_4O/CH_2O = 0·13$.
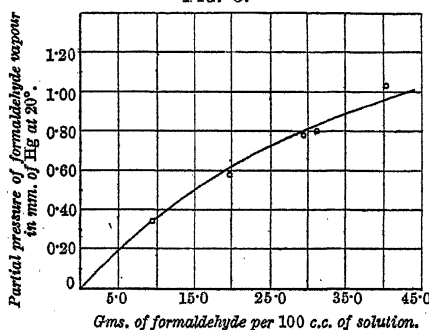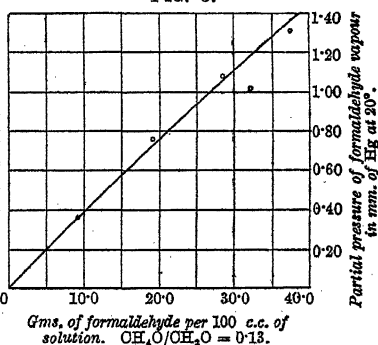
The solution containing 31·1 g. of formaldehyde per 100 c.c. was exposed, prior to the vapour-pressure determinations, at 20° in the thermostat for a number of days; the value given in the above table for the vapour pressure is the mean of several almost coincident values, *viz.*, 0·797, 0·793, 0·795 mm. of Hg, which were subsequently obtained.

In Fig. 3, the partial pressures of the formaldehyde vapour, expressed in mm. of mercury, are plotted as ordinates against the corresponding concentrations of the aqueous formaldehyde solutions in g. per 100 c.c. as abscissæ. It is seen that the partial pressure of the formaldehyde vapour is not a linear function of the formaldehyde concentration in the liquid phase (compare the relation between density and refractive index of a formaldehyde solution and the concentration of the latter as demonstrated by Ormandy and Craven, *loc. cit.*), but that the rate of increase of the partial pressure

with the concentration falls off slightly with increasing concentration of the solution.

Addition of Methyl Alcohol to Aqueous Formaldehyde Solutions at 20°.—Pure methyl alcohol, free from acetone, was added to the aqueous formaldehyde solutions treated in the manner previously described, in such amount that for all the solutions a constant small ratio CH_4O/CH_2O, *viz.*, 0·13 by weight, was preserved. As in the case of the purified aqueous formaldehyde solutions, there was again, for certain solutions, a rise in the vapour pressure values until maximum values were attained.

FIG. 4.

Litres of air passed through formaldehyde solutions.
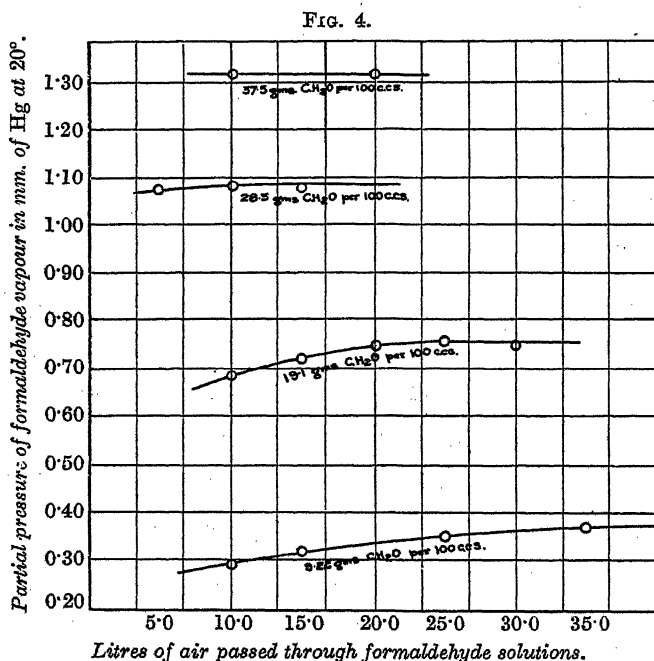
A comparison of the curves in Fig. 2 with those in Fig. 4 shows the effects of addition of small quantities of methyl alcohol to aqueous formaldehyde solutions. The partial pressure values at the outset approximate more closely to the final maximum values than is the case with uncontaminated formaldehyde solutions; the apparent equilibrium vapour pressures are raised in all cases above those previously determined; and the difference of vapour pressure due to increase in the formaldehyde concentration of the solution is more pronounced in this series of determinations. Table II gives the apparent equilibrium values of the partial pressures of these formalin solutions, together with the corresponding concen-

trations of formaldehyde vapour in the effluent air. The curve (Fig. 5) shows diagrammatically the relation of the partial pressure of the formaldehyde vapour to the formaldehyde concentration of the solution.

TABLE II.

Gms. of formaldehyde per 100 c.c. of formalin solution. CH$_4$O/CH$_2$O = 0·13	9·22	19·1	28·5	37·5
Mg. of formaldehyde vapour per litre of issuing air	0·62	1·29	1·86	2·32
Partial pressure of formaldehyde vapour in mm. of Hg	0·362	0·760	1·08	1·31

When the formaldehyde-content of the solution is expressed in g. per 100 c.c., there is a nearer approach in this case to a straight line relationship between formaldehyde-concentration and the corresponding partial pressure of formaldehyde vapour. There is a still nearer approach to a linear relationship when the formaldehyde-concentration is expressed as g. per 100 g. of solution, since the specific gravities of formalin solutions increase with concentration, the value for a 40% solution being about 1·08.

Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions at 0°.

Formalin solutions, freed from methyl alcohol, were allowed to stand at the ordinary temperature for several days and subsequently introduced into the "carburettors" (two in series were employed in these experiments at 0°). Prior to the vapour-pressure determinations, the "carburettors" were left in the thermostat over-night at 0°.

With each of the solutions examined, as increasing volumes of air were passed, the partial vapour pressures *decreased*, fairly rapidly at first, and then more slowly reached an almost constant *minimum* value. It will be remembered that the partial vapour pressure rose to an approximately constant maximum value when a purified formalin solution, after standing for a short period at 15°, was introduced into a thermostat at 20°, and air passed for the purpose of determining its partial formaldehyde vapour pressure at that temperature.

The accompanying curves, A, B, C, and D of Fig. 6, show graphically the manner in which the partial formaldehyde vapour pressures of the solutions decrease as increasing volumes of air are passed.

The apparent equilibrium values of the formaldehyde vapour pressures, that is, the constant minimum values reached when the passage of a sufficient volume of air through the solutions has

brought about apparent equilibrium conditions between liquid and vapour phases, are given in Table III, together with the corresponding concentrations of formaldehyde vapour in the effluent air.   In the case of a formaldehyde solution, containing 16 g. of formaldehyde per 100 c.c., which had been exposed at 0° in the thermostat for 12 days before the passage of air, partial pressure values were obtained which were constant from the commencement;   viz., 0·104, 0·100, 0·102 mm. of Hg. The mean of these values falls very closely to the curve in Fig. 7.

Fig. 6.

Litres of air passed through formaldehyde solutions.
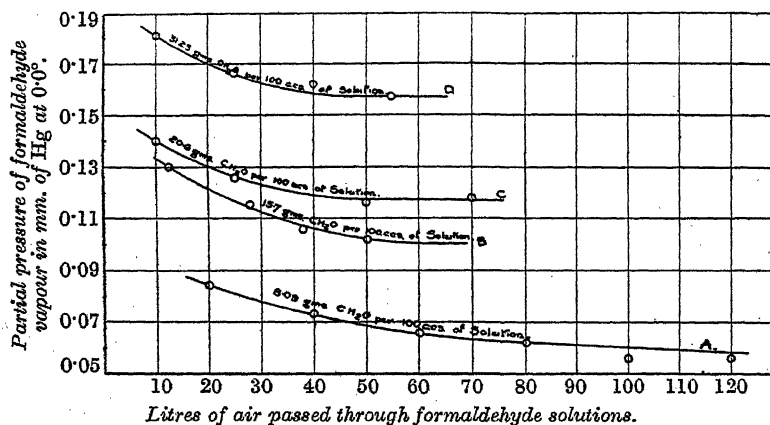
TABLE III.

Gms. of formaldehyde per 100 c.c. of formalin solution	8·09	15·68	20·63	31·25
Mg. of formaldehyde vapour per litre of issuing air	0·095	0·166	0·201	0·265
Partial pressure of formaldehyde vapour in mm. of Hg	0·056	0·102	0·118	0·157

From the data provided in Table III and from the curve of Fig. 7, it is evident that the partial formaldehyde vapour pressure is not a linear function of the concentration of the solution, but that increase in partial pressure with concentration is less pronounced at 0°. For the purpose of comparing the partial formaldehyde vapour-pressure values at 0° with those previously determined at 20°, the curves A and B are given in Fig. 8.   A is the partial formaldehyde vapour-pressure-solution-concentration curve for 0°, and B the corresponding curve, plotted on the same scale, for 20°.   For reasons cited above, it was not possible to study the vapour-pressure characteristics of formalin solutions much above 30% in strength.

The ratio Pressure of formaldehyde vapour at 0°/Pressure of

formaldehyde vapour at 20° varies progressively from 0·18 for a solution containing 30 g. of formaldehyde per 100 c.c. to 0·22 for a solution containing 5 g. of formaldehyde per 100 c.c., whilst the ratio Pressure of aqueous vapour at 0°/Pressure of aqueous vapour at 20° = 4·53/17·4 = 0·26.

From these values, it appears it is possible to obtain a more concentrated formalin solution by chilling warm air or gas, containing water vapour and formaldehyde vapour, to 0°, than by cooling the same gas to 20°. In such a process, the difference of solution strength at the two temperatures would be more pronounced in the case of the more concentrated vapours.

FIG. 7.   FIG. 8.

Gms. of formaldehyde per 100 c.c. of
solution.

Gms. of formaldehyde per 100 c.c. of
solution.
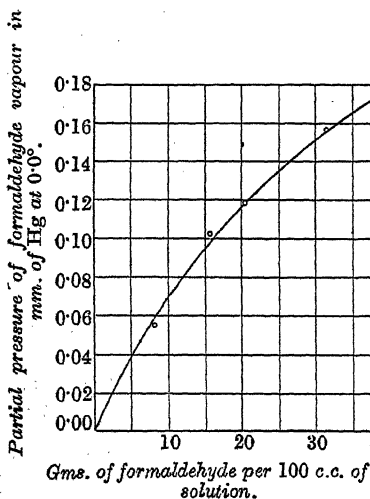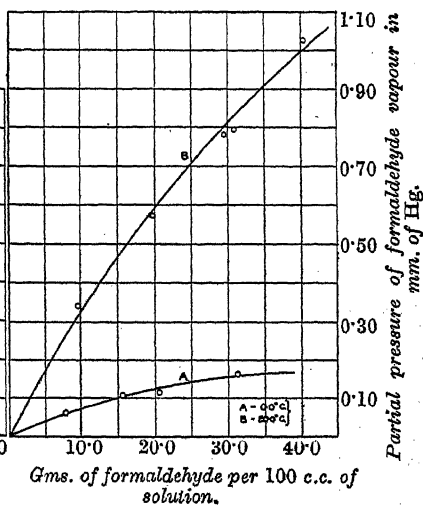
Addition of Methyl Alcohol to Aqueous Formaldehyde Solutions at 0°.—To aqueous formaldehyde solutions, methyl alcohol, free from acetone, was added in such amount that the ratio $WtCH_4O/WtCH_2O$ =0·13, this being the ratio employed in the corresponding vapour-pressure determinations at 20°. The data obtained for the solutions studied indicated that the addition of small amounts of methyl alcohol to aqueous formaldehyde solutions had very little effect on the final formaldehyde partial vapour pressure values of such solutions.

Thus from the curve (Fig. 7) it is seen that the vapour pressure of an aqueous solution containing 10·8 g. of formaldehyde per 100 c.c. in the absence of methyl alcohol is very approximately equivalent to 0·07 mm. of mercury. This value is almost identical with that obtained with a solution of corresponding strength containing a little

methyl alcohol ($CH_4O/CH_2O = 0.13$ by weight), *viz.*, 0·072 mm. of mercury. The divergence between the initial and final values is not so pronounced as in the previous instance.

Discussion of Results.

Aqueous formaldehyde solutions do not exhibit the characteristic properties of gas–water systems, but on the contrary, at the ordinary temperature, behave, from the point of view of partial vapour pressures, in a manner suggestive of solutions in water of a soluble liquid of comparatively high boiling point, *e.g.*, glycerol in water. Determinations of the apparent molecular weight of formaldehyde in its aqueous solutions, as well as the vapour tension characteristics of these solutions, indicate the existence in the dissolved state of complex molecules in addition to the simple molecules of formaldehyde. The heavier molecules of the solute may include, not only one or more polymerides of formaldehyde, but also products, complex or otherwise, derived as a result of hydration of the formaldehyde; consideration of the distinctive properties of aqueous formaldehyde solutions and evidences of the residual affinity exerted by the simple formaldehyde molecule by reason of its doubly linked oxygen atom render such a postulate feasible. A possible interpretation of the conditions existing in an aqueous formaldehyde solution may be symbolically represented as follows :—

$$[\text{Formaldehyde}] \quad \begin{array}{c} \text{complex,} \\ \text{hydrated, etc.} \end{array} \begin{array}{c} \longrightarrow \\ \longleftarrow \end{array} \begin{array}{c} CH_2O \\ \text{(simple molecules).} \end{array}$$
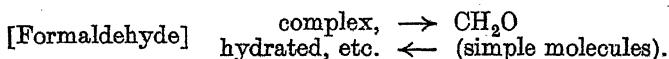
Assuming the representation provides a reasonable, although vague, conception of the equilibrium conditions within the solution, then from apparent molecular-weight determinations, vapour-pressure considerations, etc., the equilibrium at the ordinary temperature must correspond to a large excess of the heavier molecules. The partial pressure, at a particular temperature, of the formaldehyde vapour above an aqueous formaldehyde solution will be almost entirely dependent on the concentration of the simple molecular form of the aldehyde, since the heavier molecules will possess a low volatility in view of their relatively high molecular weights.

When a formaldehyde solution which had been treated for the removal of methyl alcohol was introduced into a thermostat maintained at 20°, after previously standing for several days at 15°, and air was bubbled through the solution as in the above determinations, there was an increase of the formaldehyde vapour pressure to a constant maximum value as increasing volumes of air were passed. Air passing through the solution at any particular moment takes up

formaldehyde vapour in amount corresponding to the concentration of simple formaldehyde molecules. It is assumed that the *new* equilibrium conditions between the complex and the simple molecules in solution, brought about by raising the temperature, is only gradually approached as time elapses, but that the velocity of this approach, or, in other words, the amount of simple formaldehyde produced in unit time at 20° by the transformation of the complex, is greater than the rate of removal of formaldehyde from solution under the influence of its vapour pressure; this vapour pressure being a function of the concentration of the simple molecular form of the aldehyde. Since the velocity of transformation is initially greater than that of removal, simple formaldehyde will accumulate at this temperature in excess of its original concentration. This accumulation of the simple form will exert a two-fold influence; first, by reason of its active mass in solution, it will lower the velocity of transformation of the complex, and, secondly, it will increase the velocity of the removal of formaldehyde from solution, since the latter is dependent on the concentration of the simple molecular form. In the course of time the two velocities will be equalised and the amount of formaldehyde vapour removed at 20°, by the passage of air from the solution in a given time, will reach a constant maximum value.

The gradual attainment of constant values by the formaldehyde vapour pressures at 0° can also be explained by the gradual readjustment of the equilibrium conditions between complex and simple molecules in solution, necessitated by change of temperature. A formaldehyde solution which had been exposed for several days at 20°, prior to determinations at 20° being carried out, provided a series of vapour pressure values which were almost constant from the outset. These values corresponded with a point lying very close to the curve of Fig. 3. A similar procedure in the case of a solution at 0° made it evident that in this case also the equilibrium condition had been brought about by prolonged exposure at the temperature under consideration. The latter observations lend support to the hypothesis put forward in explanation of the variations involved.

The addition of a small amount ($CH_4O/CH_2O = 0.13$) of methyl alcohol to an aqueous formaldehyde solution not only brings about, at 20°, a nearer approach of the vapour pressure determined at the outset to those determined after the passage of large volumes of air, but also produces a considerable increase (0.60 to 0.80 mm. of Hg for a solution containing 20 g. of CH_2O per 100 c.c.) in the constant maximum values eventually attained. At 0°, the equilibrium vapour pressure values were affected only very slightly by the addition of small amounts of methyl alcohol. In the course of a

further investigation, the results of which it is hoped to publish at a later date, it was found that the partial formaldehyde vapour pressure of a 15% methyl-alcoholic solution of formaldehyde at 20° was more than double that of an aqueous solution of corre-sponding strength. This would explain the relatively high values found for the formaldehyde vapour pressures of formalin solutions containing methyl alcohol, including solutions of commercial formalin.

Summary.

The partial formaldehyde vapour pressures of aqueous formalde-hyde solutions, freed from methyl alcohol, have been determined at 20° and 0° by the " dynamic " method.

After an initial exposure of a solution at 15°, an increase of the partial pressure values, as increasing volumes of air were passed until the subsequent attainment of a constant *maximum* value, was noted at 20°, whilst at 0° the continuous passage of air through a solution was shown to bring about a lowering of the partial formalde-hyde vapour pressure until a constant *minimum* value was reached.

The addition of methyl alcohol to an aqueous formaldehyde solution decreases the divergence between the initially and finally observed values of the partial formaldehyde vapour pressures, and, in the case of solutions at 20°, enhances the constant maximum value eventually obtained. Under these latter conditions, there is a nearer approach to a linear relationship between formaldehyde partial vapour pressure and concentration.

An hypothesis has been put forward to explain certain of the observations made.

Further investigations are being made on the properties of aqueous and methyl-alcoholic solutions of formaldehyde.

VI.—*The Detection of Methylamine in Presence of Excess of Ammonia.*

By P. A. VALTON.

A CONVENIENT method for the differentiation of methylamine and ammonia depends on the much greater reactivity of the former with 2 : 4-dinitrochlorobenzene; the product, 2 : 4-dinitromethyl-

aniline, is very sparingly soluble in alcohol, readily crystallised, and easily identifiable, melts sharply at 175·5°, and depresses the m. p. of 2 : 4-dinitroaniline (179°). The method can be used for detecting small quantities of methylamine in presence of excess of ammonia.

When a dilute alcoholic solution of dinitrochlorobenzene is treated with ammonia at the ordinary temperature, no dinitro-aniline separates after 20 hours, although the solution slowly becomes yellow; on the other hand, with methylamine the yellow colour develops rapidly and after 18 to 20 hours dinitromethyl-aniline crystallises out. The smallest quantities of methylamine hydrochloride which could be identified by this means were 0·005 g. when alone, and 0·008 g., 0·01 g., and 0·02 g. in presence of 0·08 g., 1 g., and 20 g., respectively, of ammonium chloride. Dimethyl-amine interferes, but the method is still applicable if the amount of dimethylamine does not exceed 10% of the methylamine. The minimum quantity of methylamine hydrochloride which could be identified was 0·02 g. in presence of 0·2 g. of ammonium chloride and 0·002 g. of dimethylamine hydrochloride, and 0·04 g. in presence of 4 g. of ammonium chloride and 0·004 g. of dimethylamine hydrochloride.

The method employed was as follows. The solution containing the methylamine and ammonium salts was introduced into a 250 c.c. flask with a Kjeldahl splash-trap, and 30 c.c. of 2N-sodium hydroxide were added together with enough water to bring the volume up to 80 c.c. The mixture was distilled into 10 c.c. of a 0·5% alcoholic solution of 2 : 4-dinitrochlorobenzene in a graduated tube, the adapter of the condenser dipping nearly to the bottom. When the volume of the solution had reached 20 c.c., the distillation was stopped and the solution left for 20 hours. The precipitated dinitromethylaniline was crystallised once from alcohol and identified by the method of mixed melting points. When the minimum amount of methylamine was used, the amount of precipitate was sometimes too small for crystallisation, but the crude product, after being washed with a little alcohol, melted above 170° and, on admixture with dinitromethylaniline, between 170° and 175°. When there was but 0·02 g. of methylamine hydro-chloride mixed with 20 g. of ammonium chloride, the former was concentrated by evaporating the solution to dryness, extracting the dry salt with 50 c.c. of hot alcohol, and using this extract in the distillation.

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VII.—*Nitro-derivatives of* o-*Cresol.*

By GEORGE PHILIP GIBSON.

THE direct nitration of o-cresol has been studied by many chemists; the chief products are 3-nitro-o-cresol and 5-nitro-o-cresol, although Spiegel, Munblit, and Kaufmann (*Ber.*, 1906, **39**, 3240) record the formation of a little 3 : 5-dinitro-o-cresol (compare Hofmann and Millar, *Ber.*, 1881, **14**, 568; Rapp, *Annalen*, 1884, **224**, 175; Schultz, *Ber.*, 1907, **40**, 4319; Wieland, Bernheim, and Böhm, *Ber.*, 1921, **54**, 1776); all workers have given the melting point 70° for 3-nitro-o-cresol, but the recorded melting point of 5-nitro-o-cresol ranges from 79° to 95°.

The author has attempted to elucidate these discordant results, although his main object has been the investigation of certain derivatives of 3-nitro-o-cresol, which were required for another research.

The greater part of the material used was prepared by Hofmann and Millar's method, although Schultz's procedure proved to be the best for mononitration owing to the ease with which the temperature and concentration can be regulated. Using the first method, if 3- and 5-nitro-o-cresols are the desired products, the conditions of nitration must be carefully adhered to, otherwise 3 : 5-dinitro-o-cresol may be the main product of the reaction.

The fact that pure 5-nitro-o-cresol is dimorphous and the presence of 3 : 5-dinitro-o-cresol and of tarry materials in the residue after the removal of the 3-nitro-o-cresol render the isolation of 5-nitro-o-cresol somewhat troublesome; although these difficulties have been overcome, the yield is poor.

5-Nitro-o-cresol forms a monohydrate melting at 30—40° (Neville and Winther, *Ber.*, 1882, **15**, 2978), which possesses properties very different from those of otherwise similar nitrocresols, which are anhydrous; crystallisation from aqueous solvents is therefore an excellent method for removing 3 : 5-dinitro-o-cresol from 5-nitro-o-cresol. Anhydrous 5-nitro-o-cresol crystallises in two forms which are interconvertible. One, the pale yellow, unstable form, which separates first, passes when it is left in the presence of solvents, crushed or rubbed, into the more stable, colourless variety.

Previous workers have usually obtained derivatives of the above-named nitro-o-cresols by the nitration of the tolyl ethers and esters (Hofmann and Millar, *loc. cit.*; Borsche, *Ber.*, 1923, **56**, 1488; Stadel, *Annalen*, 1883, **217**, 155; Reverdin, *Ber.*, 1902, **35**, 1444; 1912, **45**, 1450). In all cases, the orientation of the nitro-group is not certain and the structures of a number of these derivatives have

therefore been established by preparing the compounds directly from pure 3- and 5-nitro-*o*-cresols, and from 3 : 5-dinitro-*o*-cresol (compare Ullmann and Sané, *Ber.*, 1911, **44**, 3730; Cain and Simonsen, J., 1914, **105**, 156; Spiegel, Munblit, and Kaufmann, *loc. cit.*; Hofmann and Millar, *loc. cit.*).

In the case of derivatives of 5-nitro-*o*-cresol, ordinary methods give excellent yields, but with 3-nitro- and 3 : 5-dinitro-*o*-cresol, probably owing to the presence of two groups ortho to the reacting hydroxyl group, poor results are obtained even when the temperature is raised and the time prolonged.

For the preparation of derivatives other than the acetates (Smith and Orton, J., 1908, **93**, 1250), the dry sodium salts of 3-nitro- and 3 : 5-dinitro-*o*-cresol were heated at high temperatures with benzoyl chloride, toluene-*p*-sulphonyl chloride, methyl sulphate, and methyl toluene-*p*-sulphonate, respectively (compare Hofmann and Millar, *loc. cit.*; Cain and Simonsen, J., 1914, **105**, 156). The yields were satisfactory and the reactions took place in two directions, the proportions of the products depending on the nature of the reagent.

In the case of benzoyl chloride and toluene-*p*-sulphonyl chloride, the products were chiefly the corresponding benzoates and toluene-*p*-sulphonates with very small proportions of the corresponding chloronitrotoluene or chlorodinitrotoluene (compare Ullmann and Sané, *loc. cit.*).

In the experiments with methyl sulphate and sodium 3-nitro-*o*-tolyl oxide, the purity of the reagent seems to be the determining factor. Using pure methyl sulphate, the yield of the methyl ether is nearly theoretical, but if methyl hydrogen sulphate is present very serious complications arise and the yield may fall below 50%; sulphonic derivatives of 3-nitro-*o*-cresol and its methyl ether are produced with appreciable charring, the small amount of impurity (10% in commercial methyl sulphate) acting as an intermediary according to the equation

$$R{\cdot}H + OH{\cdot}SO_2{\cdot}OMe \longrightarrow R{\cdot}SO_2{\cdot}OMe + H_2O,$$
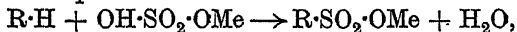
where R is $NO_2{\cdot}C_6H_2Me{\cdot}OH$ (I) or $NO_2{\cdot}C_6H_2Me{\cdot}OMe$ (II) (compare C. S. Gibson and Vining, J., 1923, **123**, 840; Simon and Frèrejacque, *Compt. rend.*, 1923, **176**, 900).

In the case of 3 : 5-dinitro-*o*-cresol, methylation takes place quantitatively in either of the above cases, because the 5-position is occupied, so that sulphonic derivatives cannot readily be formed; using methyl or ethyl toluene-*p*-sulphonate with the above dry sodium salts, good yields of the corresponding ethers are easily obtained.

EXPERIMENTAL.

Preparation of 3- *and* 5-*Nitro-o-cresols.*—A mixture of nitric acid (107 c.c.; d 1·42) and glacial acetic acid (300 c.c.) was stirred in a freezing mixture at — 15° while a mixture of o-cresol (100 g.) and glacial acetic acid (100 c.c.) was added in the course of 2 hours, when a thick magma of crystals separated. After standing 2 hours in the freezing mixture, the mass was poured into water (5000 c.c.), the crystals were separated, and submitted to steam distillation, when crude 3-nitro-o-cresol (yield 35%) containing a small proportion of 3 : 5-dinitro-o-cresol passed over; 5-nitro-o-cresol mixed with a little (10%) 3 : 5-dinitro-o-cresol then remained in the flask as an oil, which solidified when cold.

The crude distillate, m. p. 55—65°, was fractionally distilled in steam, and the various fractions were crystallised from petroleum (b. p. 80—100°). The first fractions gave deposits of deep yellow plates of nearly pure 3-nitro-o-cresol; the last gave pure 3 : 5-dinitro-o-cresol in well-defined, colourless prisms. The 3-nitro-compound may also be isolated by the crystallisation of the crude sodium salt from water.

Pure 3 nitro-o-cresol has b. p. 102—103°/9 mm. and m. p. 70°.

The residue from the steam distillation was crystallised from a large quantity of 50% alcohol, when crude 3 : 5-dinitro-o-cresol was deposited, the 5-nitro-o-cresol remaining in solution. The filtered solution was evaporated and the dark oily residue purified by distillation (b. p. 186—190°/9 mm.), by distillation in superheated steam at 180°, or by crystallisation of the sodium salt from water; in the last two cases, the monohydrate was dried at 100° and the anhydrous compound crystallised from a dry solvent such as benzene.

Anhydrous 5-nitro-o-cresol is deposited from a hot benzene solution in fine, yellow needles which, when left in the mother-liquor for a day or two, redissolve and crystallise again in large, colourless plates; the change takes place slowly from one or two centres of crystallisation, so that the line of advance of the transformation is quite distinct throughout the process. On attempting to separate the needles by filtration, they immediately fall to powder when touched or pressed, and are transformed into the plates with the correct melting point. With great care, the needles may be isolated and they remain clear for a short time, but eventually become opaque. Similar phenomena to the above occur in other solutions with more or less rapidity, but are most characteristic in benzene.

Owing to the readiness with which the unstable form is converted into the stable, both seem to melt at 96°; if great care is taken to procure the needles unchanged, the melting point is sometimes as low as 75°, but it depends on the rapidity of the heating.

On crystallisation from aqueous alcohol or acetone, 5-nitro-*o*-cresol is deposited in very fine needles of the mono-hydrate, m. p. 30—40° as stated by Neville and Winther (*Ber.*, 1882, **15**, 2978).

Preparation of 3 : 5-*Dinitro-o-cresol.*—A mixture of nitric acid (150 c.c.; *d* 1·42) and glacial acetic acid (300 c.c.) was cooled in ice and mechanically stirred while a solution of *o*-cresol (100 g.) in glacial acetic acid (100 c.c.) was gradually added. After standing at the ordinary temperature for 24 hours, the product was poured into water, the granular solid separated, and distilled in steam to remove a small amount of crude 3-nitro-*o*-cresol (yield 10%). The residue in the flask was chiefly 3 : 5-dinitro-*o*-cresol with some 5-nitro-*o*-cresol (10%) and tarry materials. After crystallisation from 50% alcohol (p. 44), the dark brown 3 : 5-dinitro-*o*-cresol was converted into the sodium salt, when the colouring matter remained in the mother-liquor and the pure salt was obtained.

Pure 3 : 5-dinitro-*o*-cresol is slightly volatile in steam (3 g. per litre) and can be recrystallised from 50% aqueous alcohol or petroleum (b. p. 60—80°).

The Sodium Salts.—As the sodium salts of the nitro-*o*-cresols are fairly readily soluble in water and appear to hydrolyse during the process of drying at 100°, they are best prepared in the pure state by treating a suspension of sodium ethoxide in boiling benzene with a benzene solution of a slight excess of the nitro-compound; the products are separated and washed with dry benzene.

Sodium 3-*nitro-o-tolyl oxide* crystallises from water in deep red plates ($+ 2H_2O$); at 100°, it sinters and then gives the anhydrous compound as a light brick-red powder (Frazer, *Amer. Chem. J.*, 1903, **30**, 309). Sample prepared with sodium ethoxide (Found : Na = 13·10. Calc. for $C_7H_6O_3NNa$, Na = 13·14%).

Sodium 5-*nitro-o-tolyl oxide* crystallises from water in yellow, hydrated needles, which, at 100°, without sintering, give a beautiful cerise, anhydrous salt. Specimen prepared with sodium ethoxide (Found : Na = 13·15%).

Sodium 3 : 5-*dinitro-o-tolyl oxide* forms a deep yellow solution and crystallises in yellow, hydrated needles which, without softening at 100°, give a deep brick-red powder. Specimen dried at 100° (Found : Na = 10·5. $C_7H_5O_5N_2Na$ requires Na = 10·46%).

Pyridine 3 : 5-*dinitro-o-tolyl oxide,* $C_{12}H_{11}O_5N_3$, separates in orange needles when a solution of 3 : 5-dinitro-*o*-cresol (2 g.) in a hot mixture of pyridine (2 g.) and benzene (10 c.c.) is cooled. It melts at 96° and gradually dissociates in the air and in solution, but it can be recrystallised from dry solvents containing a little pyridine (Found : C = 52·2; H = 4·1. $C_{12}H_{11}O_5N_3$ requires C = 52·0; H = 4·0%).

The Acetyl Derivatives.—*5-Nitro-o-tolyl acetate*, $NO_2 \cdot C_6H_3Me \cdot OAc$, was formed by the action of acetic anhydride on pure 5-nitro-o-cresol in dry pyridine at the ordinary temperature. After 12 hours, the solution was diluted with water, extracted with ether, and the extract shaken with dilute acid and then with dilute sodium hydroxide solution. The ether was evaporated and the solid residue crystallised from a mixture of petroleum (b. p. 80—100°) and acetone (large prisms) or from alcohol (needles).

This ester, m. p. 88°, is readily soluble in acetone, benzene, or chloroform, but sparingly soluble in alcohol, carbon tetrachloride, or light petroleum (Found : C = 55·3 ; H = 4·6. $C_9H_9O_4N$ requires C = 55·4 ; H = 4·6%).

3-Nitro-o-tolyl acetate was prepared by treating pure 3-nitro-o-cresol (5 g.) at the ordinary temperature with acetic anhydride (15 c.c.) containing a trace of concentrated sulphuric acid (Smith and Orton, *loc. cit.*) until the yellow colour of the nitrocresol had disappeared; water was added, the oily ester extracted with ether, the extract washed with dilute caustic soda and evaporated; the residue crystallised from alcohol in large tablets, m. p. 42°. This acetate is readily soluble in the ordinary organic solvents and crystallises well from alcohol or petroleum (b. p. 60—80°) (Found : C = 55·4 ; H = 4·5%).

3 : 5-Dinitro-o-tolyl acetate, $C_6H_2Me(NO_2)_2 \cdot OAc$, prepared in a similar manner, melts at 96° and crystallises readily from alcohol. It is fairly soluble in alcohol, acetone, benzene, or chloroform, but sparingly soluble in petroleum (b. p. 60—80°) or carbon tetrachloride (Found : C = 44·8 ; H = 3·4. $C_9H_8O_6N_2$ requires C = 45·0 ; H = 3·3%).

The Benzoyl Derivatives.—*5-Nitro-o-tolyl benzoate*,

$$NO_2 \cdot C_6H_3Me \cdot OBz,$$

was prepared in the same way as the corresponding acetate (above), a slight excess of pure benzoyl chloride being used in place of acetic anhydride.

It melts at 128°, is sparingly soluble in ether, alcohol, or light petroleum and fairly soluble in acetone, benzene, chloroform, or carbon tetrachloride (Found : C = 65·3 ; H = 4·3. $C_{14}H_{11}O_4N$ requires C = 65·4 ; H = 4·28%).

3-Nitro-o-tolyl benzoate was obtained by heating anhydrous sodium 3-nitro-o-tolyl oxide (p. 45) with pure benzoyl chloride (2 mols.) for 1 hour at 120°. The product was treated in the cold with a mixture of pyridine, water, and ether; the ethereal solution was shaken successively with acid and with dilute alkali and finally evaporated; the residue crystallised from alcohol or petroleum (b. p. 60—80°) in needles, m. p. 42°, b. p. 218—220°/9 mm. This

ester is soluble in the usual organic solvents with the exception of petroleum (b. p. 60—80°) (Found : C = 65·4; H = 4·2%).

3 : 5-*Dinitro*-o-*tolyl benzoate*, $C_6H_2Me(NO_2)_2 \cdot OBz$, m. p. 132°, prepared in a similar manner from sodium 3 : 5-dinitro-o-tolyl oxide, crystallises readily from acetone, alcohol, or benzene; it is sparingly soluble in alcohol, ether, or light petroleum, but easily soluble in acetone, benzene, chloroform, or carbon tetrachloride (Found : C = 55·7; H = 3·4. $C_{14}H_{10}O_6N_2$ requires C = 55·6; H = 3·3%).

The Toluene-p-*sulphonyl Derivatives.*—5-*Nitro*-o-*tolyl toluene*-p-*sulphonate*, $NO_2 \cdot C_6H_3Me \cdot O \cdot SO_2 \cdot C_7H_7$, obtained as in the case of the corresponding benzoate (p. 46), using toluene-p-sulphonyl chloride, crystallises from alcohol, petroleum (b. p. 60—80°), or carbon tetrachloride in indefinite plates, m. p. 107°. It is sparingly soluble in alcohol or light petroleum, but fairly soluble in acetone, benzene, chloroform, or , carbon tetrachloride (Found : S = 10·5. $C_{14}H_{13}O_5NS$ requires S = 10·4%).

3-*Nitro*-o-*tolyl toluene*-p-*sulphonate* was prepared by treating sodium 3-nitro-o-tolyl oxide (1 mol.) with pure toluene-p-sulphonyl chloride (2 mols.) : * the conditions and method of isolation were the same as those described in the case of the benzoate (p. 46).

The compound melts at 66° and boils at 257°/11 mm. with decomposition, but distils unchanged at 205—210°/0·5 mm.; it crystallises well from alcohol, in which it is sparingly soluble, and dissolves freely in acetone, benzene, chloroform, or carbon tetrachloride (Found : S = 10·2%).

The corresponding toluene-p-sulphonate from 3 : 5-dinitro-o-cresol, which has already been isolated by Ullmann and Sané (*Ber.*, 1911, **44**, 3730), can be prepared in a similar manner.

3-Nitro-o-chlorotoluene is formed in very small quantities by the action of benzoyl or toluene-p-sulphonyl chloride on sodium 3-nitro-o-tolyl oxide and can be isolated by steam distillation of the crude reaction mixture, when a pale yellow, pleasant-smelling oil passes over (compare Holleman, *Rec. trav. chim.*, 1908, **27**, 456).

In a similar manner, sodium 3 : 5-dinitro-o-tolyl oxide yields the corresponding 3 : 5-dinitro-o-chlorotoluene (m. p. 63°), which was oxidised to 3 : 5-dinitro-o-chlorobenzoic acid (m. p. 238°).

The Methyl Ethers.—5-*Nitro*-o-*tolyl methyl ether*, m. p. 64° (Cain and Simonsen, *J.*, 1914, **105**, 2390, give m. p. 62°), crystallises readily in needles from alcohol or petroleum, but is freely soluble in acetone, chloroform, carbon tetrachloride, or benzene. On

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* The commercial compound was dried in a vacuum at 100° and dissolved in hot petroleum (b. p. 60—80°), the tarry material filtered off, the solvent removed, and the residue distilled under reduced pressure; b. p. 138—139°/9 mm.

oxidation with boiling dilute permanganate, 5-nitro-o-methoxy-benzoic acid (m. p. 150°) was obtained in theoretical yield.

3-Nitro-o-tolyl methyl ether was obtained by heating sodium 3-nitro-o-tolyl oxide (1 mol.) at 120° with pure methyl sulphate (2 mols.) for 2 hours. The dark-coloured reaction mixture was submitted to distillation in steam, the volatile oil extracted with ether, and the 3-nitro-o-cresol removed with dilute alkali. The ethereal solution was evaporated, the residue distilled under 10 mm., and the product (b. p. 121—122°) dissolved in petroleum (b. p. 60—80°); at —15°, the solution deposited 3-nitro-o-tolyl methyl ether in large needles, m. p. 30°.

The residue from the steam distillation of the methyl ether, treated with calcium carbonate, gave a mixture of calcium nitro-cresolsulphonates (p. 43) together with sodium carbonate, but the acids could not be separated by the fractional crystallisation of various inorganic and organic salts which were tried.

3 : 5-Dinitro-o-tolyl methyl ether (m. p. 72°) can be prepared under the conditions just described; the yield is good. 3-Nitro-o-tolyl methyl and ethyl ethers and the corresponding methyl and ethyl derivatives of 3 : 5-dinitro-o-cresol were also prepared by heat-ing the requisite dry sodium salts with methyl or ethyl toluene-p-sulphonate * in a similar manner. The yields were good, and the products had the properties given in the literature.

VIII.—Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. Part II. Mixtures of More than One Gas and Air.

By ALBERT GREVILLE WHITE.

LE CHATELIER has put forward a formula connecting the limit for the propagation of flame in a mixture containing two inflammable

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* Pure toluene-p-sulphonyl chloride (50 g.; p. 47) was suspended in methyl (or ethyl) alcohol (100 c.c.), well-stirred, and 20% caustic soda (10% in excess of 1 mol.) gradually added with cooling; the oil which took the place of the solid was separated with ether, and the extract was washed with water, dried with sodium sulphate, and evaporated. The residue was crystallised from alcohol at —15°. B. p. of methyl ester, 146—147°/9 mm.; of ethyl ester, 165—166°/9 mm.

gases and air with the limits for the two inflammable gases taken
separately.   When generalised, it becomes

$$n_1/N_1 + n_2/N_2 + n_3/N_3 + \quad . \quad . \quad . \quad . \quad . \quad = 1,$$

where n_1, n_2, n_3, . . . are the percentages of different combustibles
found in the final limit mixture, and N_1, N_2, N_3, . . . are the per-
centages of the same combustibles required to give limit mixtures
when each is mixed separately with air.   The formula is additive
in character, and indicates that if any number of limit mixtures are
mixed, the resulting mixture will be a limit mixture.   It is simple,
but unlikely to be universally true.

It has been shown (J., 1922, **121**, 2561) that the formula enables
the lower limits of binary mixtures to be calculated fairly accurately
from the limits of the pure vapours, except for mixtures containing
carbon disulphide, where agreement over a portion of the range was
only obtained when an artificial figure was used for the limit of
carbon disulphide.   At the upper limit of downward propagation
the mixtures also followed Le Chatelier's rule, except mixtures
containing carbon disulphide, but notable discrepancies were
sometimes found for other directions of propagation.   These could
be traced to anomalous behaviour of one of the vapours.   Thus
the formula was clearly inapplicable to a vapour giving a cool flame,
and by the suitable choice of a second vapour the propagation range
of ether–second vapour–air was divided into two, the mixtures
having thus four limits instead of two.

Coward, Carpenter, and Payman (J., 1919, **115**, 27, 31), who deal
only with propagation upwards, conclude that the limits of inflam-
mability, in air, of mixtures of hydrogen, carbon monoxide and
methane, taken two at a time or all together, as well as the limits
of coal gas, may be calculated by using Le Chatelier's formula.
Other workers have drawn the same conclusion, but since the
amount of experimental work was small, further experiments
appeared to be desirable, as any radical departure from the formula
might throw light on the method of propagation at the limit of the
individual gases used.

The experimental arrangements were identical with those used
previously (J., 1924, **125**, 2387), except that the tubes were 5 cm. in
diameter unless some other size is specified.   The work was all
carried out within the range of $17° \pm 4°$, and usually between 15°
and 19°.   The results are given in Tables I and II.   Limits are
given as percentages by volume throughout, and percentage errors
are calculated as percentages of the amount of inflammable gas in
the limit mixture.

TABLE I.

Showing the ranges of propagation of flame for mixtures of pairs of inflammable gases and air, and the deviations from Le Chatelier's formula.

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% H₂.	% CH₄.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
0	100	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
10	90	5·50 to —	5·24 to	— 5	—				
25	75	4·75 to 18·5	5·02 to 17·9	+ 6	— 3	6·75 to 16·5	6·65 to 16·7	— 1	+ 1
50	50	4·45 to 26·1	4·69 to 23·9	+ 5	— 8	7·35 to 22·3	7·29 to 22·5	— 1	+ 1
75	25	4·15 to 38·3	4·40 to 36·2	+ 6	— 6	8·10 to 34·3	8·05 to 34·5	— 1	+ 1
100	0	4·15 to 74·5	—	—	—	9·00 to 74·0	—	—	—
% H₂.	% NH₃.								
0	100	16·1 to 26·6	—	—	—	—	—	—	—
25	75	8·65 to 34·5	9·36 to 31·7	+ 8	— 8	16·2 to 30·5	*22·1 to *25·5		
50	50	6·10 to 45·2	6·60 to 39·2	+ 8	—13	12·5 to 41·0	*20·5 to *28·4		
75	25	4·75 to 57·0	5·10 to 51·4	+ 7	—10	10·5 to 55·2	*21·0 to *31·3		
100	0	4·15 to 74·5	—	—	—	9·00 to 74·0	—	—	—
% C₂H₄.	% H₂.								
0	100	4·15 to 74·5	—	—	—	9·00 to 74·0	—	—	—
5	95	— to 56·0	— to 70·2	—	+25				
10	90	4·00 to —	4·02 to	0	—	7·95 to —	7·74 to	— 3	—
25	75	3·95 to 42·0	3·84 to 56·9	— 3	+35	6·85 to 34·0	6·39 to 37·8	— 7	+11
50	50	3·70 to 36·5	3·57 to 46·0	— 4	+26	5·35 to 23·5	4·96 to 25·4	— 7	+ 8

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% C_2H_4.	% H_2.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
75	25	3·45 to 33·5	3·33 to 38·6	− 3	+15	4·15 to 18·9	4·05 to 19·1	− 2	+ 1
100	0	3·13 to 33·3	—	—	—	3·42 to 15·3	—	—	—
% C_2H_2.	% H_2.								
0	100	4·15 to (4·15)	—	—	—	9·00 to —	—	—	—
25	75	3·55 to (3·50)	3·60 to —	+ 2	—	6·02 to —	5·79 to —	− 4	—
40	60	3·34 to —	3·35 to —	0	—				
50	50	3·24 to (3·20)	3·19 to —	− 2	—	4·42 to —	4·27 to —	− 3	—
57	43	3·49 to —	3·10 to —	−11	—				
60	40	— to (3·39)	—	—	—				
65	35	3·32 to —	2·99 to —	−10	—				
75	25	3·11 to (3·12)	2·87 to —	− 8	—	3·40 to —	3·38 to —	− 1	—
85	15	2·93 to —	2·76 to —	− 6	—				
100	0	2·60 to (2·60)	—	—	—	2·80 to —	—	—	—
% C_3H_4.	% CH_4.								
0	100	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
25	75	4·75 to 16·1	4·57 to 16·6	− 4	+ 3	5·23 to 13·7	5·11 to 13·7	− 2	0
50	50	4·22 to 19·5	3·96 to 20·0	− 6	+ 3	4·55 to 14·0	4·39 to 14·2	− 4	+ 1
75	25	3·72 to 25·0	3·50 to 25·0	− 6	0	4·05 to 14·8	3·84 to 14·7	− 5	− 1
100	0	3·13 to 33·3	—	—	—	3·42 to 15·3	—	—	—

The figures in brackets in Table I are lower-limit determinations carried out in tubes 7·5 cm. in diameter. Those marked with an asterisk are the values of the propagation range downwards for ammonia–air mixtures as calculated from the ranges found for the various ammonia–hydrogen–air mixtures.

TABLE II.

Showing the ranges of propagation of flame for mixtures of pairs of inflammable gases and air, and the deviations from Le Chatelier's formula.

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% CH₄.	% H₂S.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
0	100	4·40 to 44·5	—	—	—	6·05 to 19·8	—	—	—
10	90	5·15 to —	4·48 to —	−13	—	6·50 to —	6·06 to —	− 7	—
15	85	— to 36·3	— to 33·8	—	− 7	—	—	—	—
25	75	5·75 to 33·0	4·61 to 29·1	−20	−12	6·90 to 19·1	6·07 to 17·6	−12	− 8
40	60					— to 17·2	— to 16·5	—	− 4
50	50	6·03 to 28·8	4·85 to 21·6	−20	−25	7·00 to 15·9	6·08 to 15·9	−13	0
60	40	— to 26·1	— to 19·6	—	−25				
65	35					— to 14·2	— to 15·0	—	+ 6
67·5	32·5	— to 18·6	— to 18·3	—	− 2				
75	25	5·80 to 15·7	5·11 to 17·2	−12	+10	6·75 to 13·6	6·10 to 14·4	−10	+ 6
100	0	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
% H₂S.	% H₂.								
0	100	4·15 to 74·5	—	—	—	9·0 to 74·0	—	—	—
10	90					— to 50·0	— to 58·1	—	+16
15	85	— to 46·0	— to 67·7	—	+47	— to 45·5	— to 52·5	—	+15
25	75	4·27 to 41·3	4·21 to 63·8	− 1	+54	8·43 to 38·7	8·02 to 43·9	− 5	+13
50	50	4·78 to 40·0	4·27 to 55·7	−11	+39	7·85 to 29·0	7·24 to 31·2	− 8	+ 8

Composition of combustible in mixture by vol.		Upward propagation.				Downward propagation.			
		Range.		% Deviation at		Range.		% Deviation at	
% H₂S.	% H₂.	Found.	Calc.	Lower limit.	Upper limit.	Found.	Calc.	Lower limit.	Upper limit.
75	25	5·03 to 40·4	4·34 to 49·5	−14	+23	6·95 to 23·0	6·59 to 24·2	− 5	+ 5
90	10	4·72 to —	4·37 to —	− 7	—				
100	0	4·40 to 44·5	—	—	—	6·05 to 19·8	—	—	—
% H₂S.	% C₂H₂.								
0	100	2·60 to —	—	—	—	2·80 to —	—	—	—
25	75	2·99 to —	2·90 to —	− 3	—	3·23 to —	3·23 to —	0	—
50	50	3·44 to —	3·27 to —	− 5	—	3·88 to —	3·83 to —	− 1	—
75	25	4·04 to —	3·75 to —	− 7	—	4·80 to —	4·69 to —	− 2	—
90	10	4·36 to —	4·11 to —	− 6	—				
100	0	4·40 to —	—	—	—	6·05 to —	—	—	—
% C₂H₂.	% CH₄.								
0	100	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—
10	90	— to 15·7	— to 15·5	—	− 1				
25	75	4·40 to 23·4	4·25 to 17·9	− 3	−24	4·85 to 15·7	4·72 to 16·5	− 3	+ 5
30	70	— to 39·5	— to 18·9	—	−52				
40	60	— to 47·0	— to 21·2	—	−55				
50	50	3·67 to 47·0	3·51 to 24·1	− 4	−49	3·98 to 20·4	3·84 to 21·9	− 4	+ 7
75	25	3·07 to 58·0	2·99 to 36·8	− 3	−37	3·27 to 31·2	3·24 to 32·6	− 1	+ 4
100	0	2·60 to 78·0	—	—	—	2·80 to 63·5	—	—	—

Composition of combustible in mixture. by vol.		Upward propagation.		% Deviation at		Downward propagation.		% Deviation at	
% CH₄.	% C₅H₁₂.	Range. Found.	Calc.	Lower limit.	Upper limit.	Range. Found.	Calc.	Lower limit.	Upper limit.
0	100	1·43 to 8·00	—	—	—	1·49 to 4·56	—	—	—
20	80	— to 8·85	to 8·77	—	− 1				
25	75	1·75 to —	1·75 to —	0	—	1·84 to 5·30	1·84 to 5·45	0	+ 3
50	50	2·23 to 9·65	2·26 to 10·25	+ 1	+ 6	2·38 to 6·50	2·40 to 6·78	+ 1	+ 4
75	25	3·15 to 11·35	3·19 to 11·92	+ 1	+ 5	3·47 to 8·75	3·45 to 8·98	− 1	+ 3
100	0	5·40 to 14·25	—	—	—	6·12 to 13·25	—	—	—

Discussion of Results.

The figures of Table I show that for propagation downwards the deviations from Le Chatelier's rule are not important except for hydrogen–ethylene–air and hydrogen–ammonia–air mixtures. Hydrogen and ethylene appear to hinder one another's burning at the limit, as the calculated range is wider than that observed. The results for propagation upwards show that at both upper and lower limits the presence of hydrogen makes propagation easier than might have been expected when the second inflammable gas is methane or ammonia. This does not apply to mixtures containing acetylene or ethylene, the discrepancies shown by the upper-limit figures for mixtures of the latter being striking. The corresponding deviations at the lower limit are small, but when considered in conjunction with the corresponding ones for mixtures containing methane or ammonia, they appear to indicate a distinct hindering effect when either ethylene or acetylene is mixed with hydrogen at the limit. In addition, a somewhat curious change of sign occurs for the deviations from Le Chatelier's rule at the lower limit in both methane–hydrogen–air and acetylene–hydrogen–air mixtures. Thus in Fig. 1, which shows the lower-limit figures observed and calculated for the latter mixtures, the experimental curve consists of two parts, one portion, representing mixtures containing an excess of hydrogen, being slightly below, and the other portion distinctly above, the curve of calculated values. When the percentage of acetylene in the combustible gas in the limit

mixture is changed from 50% to 57%, the limit rises from 3·24% to 3·49%, despite the fact that the limit for acetylene is considerably lower than that for hydrogen. Considerable difficulty was experienced in determining the limit for the 50% mixture. Mixtures containing an amount of combustible not less than 3·24% sometimes propagated flame throughout the length of the tube, whilst mixtures containing more than 3·24% but less than 3·40% often failed to do so. The difficulty, which was also encountered, although in a less degree, when determining the corresponding limit for the

FIG. 1.

Showing the lower limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for propagation upwards in acetylene–hydrogen–air mixtures.

Percentage of acetylene (by volume) in the combustible used.
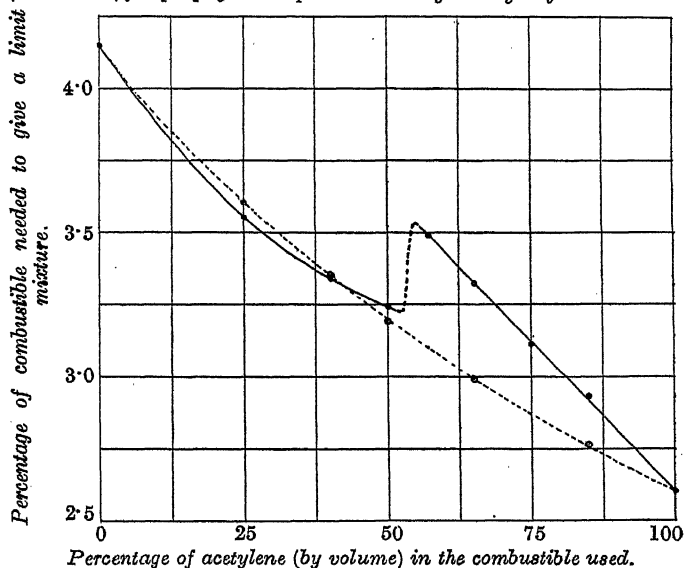
mixture containing 75% of methane and 25% of hydrogen, was overcome in each case by making numerous trials with each mixture and taking as the limit mixture that containing least combustible in which a flame was propagated throughout the tube, despite the fact that a mixture containing the same percentage, or even a greater percentage of combustible, had failed to propagate flame; if one of several similar mixtures propagated flame farther than the others, that mixture was always burning with a flame more closely resembling that of hydrogen than the others. It is thus apparently only when initiated so as to give the hydrogen type of flame that the true limit mixture propagated flame. The analogy with the state of things sometimes found when a cool flame can be propagated

in certain mixtures is at once seen.   In the latter case, an ordinary flame goes out during its passage along a limit tube, whilst a cool flame always reaches the far end.   When a tube 7·5 cm. in diameter was used, there was little difficulty in producing the hydrogen type of flame every time in the mixtures referred to above, and the limits obtained provided useful confirmation of those obtained in 5 cm. tubes.   The values in brackets (7·5 cm. tubes) in Table I. show that the difference between the 5 cm. and the 7·5 cm. results is nowhere important.   The agreement for methane–hydrogen–air mixtures was just as good.   The observation that the flame for mixtures shown along part of the curve in Fig. 1 was always of the hydrogen type, whilst that found for those on the other portion more nearly resembled the ordinary lower-limit flame, suggests a possible explanation of the results obtained.   In Part I it is shown that, for upward propagation at the lower limit, the hydrogen flame itself and the low calorific value of the limit mixture are quite out of the ordinary.   Apparently hydrogen is able to pass on its peculiar properties, in part at any rate, to mixtures with other gases, but these properties are damped out by excessive amounts of the second gas.   With acetylene–hydrogen–air, there is, between 50% and 57% of acetylene, a limit—that at which the amount of acetylene becomes sufficient to damp out the peculiar hydrogen flame.   This point does not appear to be clearly marked with ethylene–hydrogen–air mixtures, but is fairly easily seen for methane–hydrogen–air mixtures, although the range of the " ordinary " flame here appears to be small.   It is unexpected to find that the substitution of 10% of hydrogen for methane causes an increase in the limit from 5·40% to 5·50%.   The analogy with the cool flame is well maintained, inasmuch as it takes differing amounts of different gases to suppress the hydrogen flame.   That the phenomenon is not confined to the mixtures examined is shown by certain results of Coward and his collaborators (loc. cit.).   They state : " The most striking anomaly was shown by the mixture containing 10 per cent. of hydrogen and 90 per cent. of carbon monoxide, where the large difference was in the opposite direction to that normally noted," but suggest no explanation.

The second part of the acetylene–hydrogen–air curve is so distinct from the first as to lead one to attempt to obtain from it some idea as to what the lower limit upwards would be for hydrogen if its own peculiar flame could be suppressed.   Assuming Le Chatelier's rule to hold and making use of the value for 75% of acetylene and 25% of hydrogen, a figure between 7 and 8% is obtained.   This is reasonably near the value for propagation downwards, but little reliance can be placed on it for two reasons.   In the first place

Le Chatelier's rule is not followed closely by these gases even for propagation downwards, and, in the second, a different and lower value would be obtained by using the figures for methane–hydrogen–air. Nevertheless, any figures obtained by extrapolation would be likely to be minimum values, so that the figure is certainly suggestive.

As ammonia does not propagate flame downwards at the ordinary temperature, the ammonia–hydrogen–air values have been utilised to calculate hypothetical values for the ammonia limits. The lower-limit results are reasonably near one another, but there is a large increase observable in the upper-limit values as the percentage of hydrogen in the mixture increases. The values obtained appear to point to the fact that for downward propagation at the upper limit considerable deviations from Le Chatelier's rule take place for these mixtures, the experimental values being greater than those calculated.

The results given in Table II confirm those of Table I in many respects, but on the whole the deviations of the experimental values from those calculated appear to be greater. The deviations are again generally greater for upper-limit results than for lower-limit figures, and greater for upward propagation than for propagation downwards. The work on lower-limit mixtures containing both methane and hydrogen sulphide reveals unexpectedly large deviations from the rule, so that these two inflammable gases appear to hinder one another considerably in propagating flame at the limit. Methane appears to give much more normal results when used in conjunction with carbon monoxide, hydrogen, certain organic vapours, and even with acetylene and ethylene. Accordingly lower-limit mixtures containing hydrogen sulphide and acetylene were tested. Contrary to expectation, these results were far nearer those calculated, the deviations for propagation downwards being exceedingly small. Fair deviations were found for mixtures containing hydrogen sulphide and hydrogen.

The upper-limit results are best examined from the point of view of the curves shown in Figs. 2 to 4, which show both experimental and calculated values. The deviations of the experimental from the calculated values for methane–hydrogen sulphide–air mixtures (Fig. 2) are sometimes large, but the most interesting point is the fact that for both directions of propagation the experimental and theoretical curves cut one another. For downward propagation, about as much of the experimental curve lies above the theoretical as below, but this is not the case for upward propagation. It should also be noticed that whilst the addition of some methane to a hydrogen sulphide–air mixture hinders propagation at the lower limit, it seems to promote propagation at the upper limit.

The values for hydrogen sulphide–hydrogen–air mixtures show that for both upper and lower limit mixtures these gases propagate flame relatively more easily singly than when both are present in a mixture. Fig. 3 shows that at the upper limit this effect is much more marked for upward than for downward propagation. For mixtures in which more than 80% of the combustible is hydrogen, the limits for both directions of propagation are almost identical, but for mixtures poorer in hydrogen the two curves are quite different. The experimental and the theoretical curves are of very

FIG. 2.

Showing the upper limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for methane–hydrogen sulphide–air mixtures. D denotes downward propagation, U propagation upwards.

Percentage of combustible needed to give a limit mixture.

Percentage of methane in the combustible used.
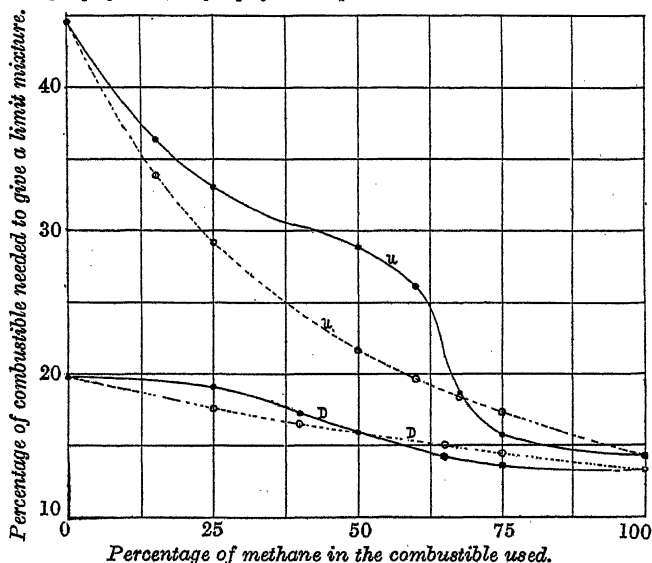
similar form for propagation downwards, but for upward propagation the major portion of the experimental curve is nearly horizontal. Experimental difficulty was encountered when the upper limit was being determined for mixtures in which 75% of the inflammable gas was hydrogen and the remainder hydrogen sulphide. The limit figure obtained was dependent on the flame starting up the tube, the type of flame being presumably controlled by the igniting mechanism. It was difficult to control efficiently the type of flame produced, and the limit figure was determined as in the case of acetylene–hydrogen–air mixtures (p. 55).

The values for the upper limit for methane–acetylene–air mixtures

FIG. 3.

Showing the upper limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for hydrogen sulphide–hydrogen–air mixtures. D denotes downward propagation, U propagation upwards.

Percentage of hydrogen sulphide in the combustible used.
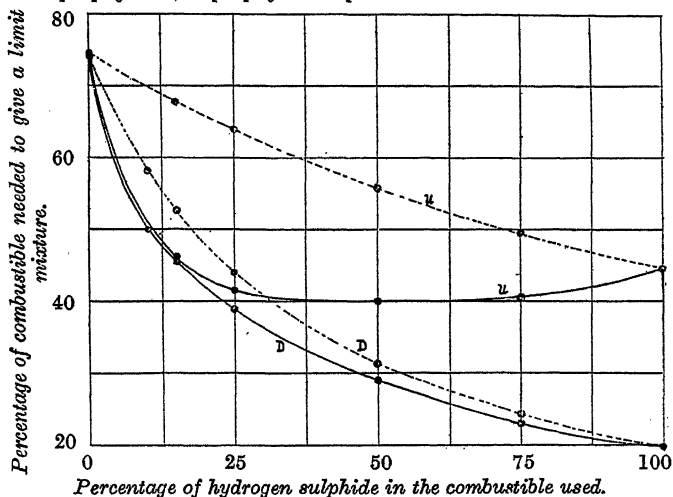
FIG. 4.

Showing the upper limits observed (full line) and calculated from Le Chatelier's rule (dotted line) for methane–acetylene–air mixtures. D denotes downward propagation, U propagation upwards.

Percentage of methane in combustible used.
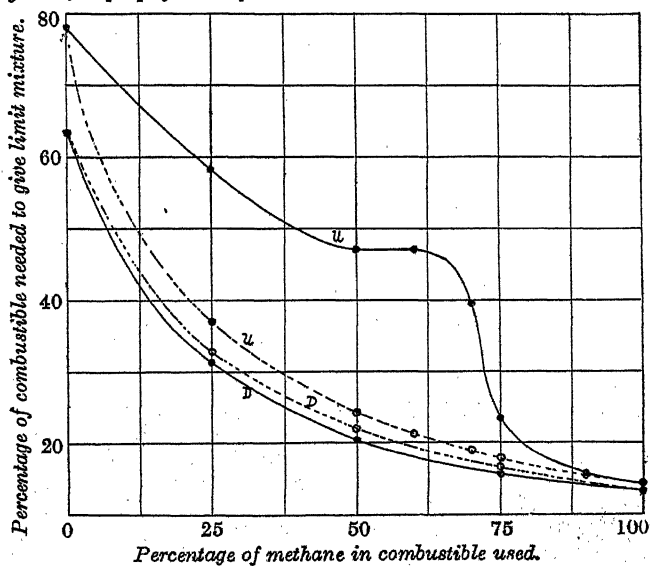
(Fig. 4) are not far from those calculated for downward propagation, the latter being always the greater. For upward propagation, the differences between the two sets of results are far greater, and are in the opposite direction, as the experimental figures are the greater, showing that propagation appears relatively easier when the two gases are present at the limit than when one is burning alone. The sudden fall in the curve appeared to coincide with a change in the appearance of the flame passing through the mixture. It does not appear difficult to account partly for the left-hand portion of the curve. The high values of acetylene upper limits are largely due to the endothermicity of this compound, which can provide much of the heat necessary for the propagation of flame without using up a corresponding amount of oxygen. The reduction of the limit on replacing some acetylene by methane would increase the amount of oxygen in the mixture, and this might easily intensify the abnormal effect due to acetylene.

A comparison of the present results with those obtained with vapour–air mixtures (loc. cit.) is not without interest. Outside mixtures containing carbon disulphide, for any two vapours tested, the lower limits and the upper limit for downward propagation for any mixture could be calculated from the limits of the vapours taken singly to an accuracy of about $\pm 2\%$. With the gases now examined, an error of five times this amount, or even more, would often be made under the same conditions. For propagation upwards, both sets of results show that calculation is liable to give results far from those found experimentally.

Payman (J., 1923, 123, 412) suggests that as the rate of reaction in a mixture must depend on the concentration of the reacting gases, speeds of flame in mixtures should be slightly slower than those calculated, and a similar divergence should be observable for limit mixtures. He gives figures supporting this view. The effect of mass action should be to reduce the upper limit of a mixture below that calculated. An examination of the eight series of upper-limit results determined in this investigation shows that, in the main, for downward propagation, in four cases the experimental figures are distinctly lower than those calculated, whilst in one series they are distinctly higher. For propagation upwards, four out of the eight series of experimental figures appear to be higher, and four lower, than those calculated. Mass action thus appears to be only one, and often not the most important one, of the factors responsible for divergencies from the calculated values for upper limits in the mixtures examined.

Summary.

Limits for the propagation of flame have been determined in various mixtures of pairs of combustible gases and air. The results tend to show that in most cases a fair approximation to the value of the limit for a binary mixture can be obtained from the limits for the separate gases by the use of Le Chatelier's rule. The approximation is generally better for lower than for upper limits, and better for downward propagation than for propagation upwards.

The deviations from this rule are considerably greater for the gas mixtures examined than for normal vapour mixtures, but no rule can be given for the direction of the deviation from the calculated values. For gas, as for vapour mixtures, the *type* of flame started sometimes determines whether propagation occurs or no.

IX.—*Solubility of Bi-bivalent Salts in Solutions Containing a Common Ion.*

By OSWALD JAMES WALKER.

THE investigation of the solubility of salts in dilute solutions of salts with common ions has been confined mainly to the following cases : 1. Uni-univalent salt + univalent common ion. 2. Uni-bivalent salt + univalent common ion. 3. Uni-bivalent salt + bivalent common ion.

It was shown by Noyes and his co-workers (*J. Amer. Chem. Soc.*, 1911, **33**, 1643, 1807) that in cases (1) and (2) the solubility decreases rapidly, and the curve obtained by plotting solubility against concentration of added salt is roughly of the form to be expected from the solubility product principle. In case (3), where a salt with a common bivalent ion is added, the decrease in solubility is much less than what would be expected from that principle, and if the saturating salt is sufficiently soluble the common ion may actually bring about an increase in the solubility. Fewer cases have been studied in which the saturating salt is bi-bivalent, and such cases as have been examined (*e.g.*, Harkins and Paine, *J.Amer. Chem. Soc.*, 1919, **41**, 1162) have shown that here also the solubility decrease brought about by the common ion is less than what would be expected. More recently there has been a tendency to reject

the conductivity method of calculating ionic concentrations, which was the method used in applying the solubility product principle, and the question of solubility effects has been approached from a different point of view based on thermodynamic considerations which involve the principles of the inter-ionic attraction theory.

With a view to get further evidence concerning the solubility effects in the system bi-bivalent salt + bivalent common ion, the solubilities of several salts have been investigated. For this purpose, the succinates and malonates of the alkaline-earth metals afford a suitable range of concentrations. The solubilities of the various salts considered, expressed in gram-molecules per 1000 grams of water, varied between 0·016 and 0·082 weight molar, whilst the total salt concentration did not exceed 0·1 weight molar, except in the case of calcium succinate as saturating salt, with which a maximum of about 0·3 weight molar was reached.

<div align="center">EXPERIMENTAL.</div>

The saturating salts were prepared from pure reagents by precipitation, thorough washing, and drying at the temperature requisite to give the anhydrous salt. Sodium and magnesium succinates were obtained by crystallisation from neutralised succinic acid solutions and were recrystallised several times. Analysis confirmed the purity of the salts thus obtained.

The solubility determinations were carried out in 100 c.c. Jena conical flasks, closed with rubber stoppers and provided with rubber caps. Excess of the saturating salt and a weighed quantity of the other salt were added to a known weight of water in the flask, and the mixture was rotated in a thermostat kept at $25^\circ \pm 0\cdot1^\circ$ until equilibrium had been reached (about 30 hours). The solution, after standing in the thermostat for an hour, was filtered upward by suction through a small filter paper into a weighed flask, which was also in the thermostat. After weighing, the solution was carefully washed out into a beaker and the solubility was obtained by determining gravimetrically the amount of the metallic radical of the saturating salt. Barium was estimated in most cases as sulphate, but in presence of calcium, Browning's method (*Amer. J. Sci.*, 1892, [iii], **43**, 314), depending on the difference in solubility of the nitrates in amyl alcohol, was employed. Calcium was precipitated as oxalate and weighed as sulphate, the precipitation, in presence of magnesium, being carried out twice. Strontium was precipitated as carbonate and weighed as sulphate. In the case of strontium malonate + strontium chloride, the chloride in the solution was determined gravimetrically as silver chloride, and the amount of strontium as malonate was determined by subtraction of

the strontium present as chloride from the total strontium. Independent solubility determinations gave results agreeing within 0·5%.

The results are shown in Table I, s being the solubility, expressed in gram-molecules per 1000 grams of water, corresponding to the weight-molar concentration, c, of added salt; s_0 is the solubility

TABLE I.

s.	c.	s.	c.	s.	c.
Ba succ. + Na succ.		Sr mal. + SrCl$_2$.		Ba succ. + Mg succ.	
$s_0 = 0\cdot01570$.		$s_0 = 0\cdot03050$.		$s_0 = 0\cdot01570$.	
0·01307	0·00798	0·02523	0·01828	0·01397	0·00770
0·01154	0·01575	0·02349	0·03103	0·01294	0·01538
0·00987	0·03149	0·02019	0·06149	0·01155	0·03074
0·00913	0·04726			0·01065	0·04620
				0·01024	0·06149
Sr succ. + Na succ.		Ca succ. + Na succ.		Ba succ. + Ca succ.	
$s_0 = 0\cdot02013$.		$s_0 = 0\cdot08252$.		$s_0 = 0\cdot01570$.	
0·01740	0·00938	0·08013	0·00826	0·01383	0·00798
0·01535	0·01875	0·07103	0·0506	0·01275	0·01597
0·01322	0·03751	0·06495	0·1014	0·01155	0·03193
0·01221	0·05582	0·06138	0·1526		
0·01143	0·07457	0·05759	0·2560		

Calcium succinate + Magnesium succinate.
$s_0 = 0\cdot08252$.

s	0·07769	0·07474	0·07340	0·07173	0·07087
c	0·04121	0·06179	0·08230	0·1231	0·1631

of the saturating salt in pure water. The solubility effects, however, can be more easily compared by means of the ratios s/s_0 and c/s_0, which express respectively the concentrations of the saturating salt and of the added salt in terms of the solubility of the former in pure water. These ratios correspond to the terms "fractional solubility" and "fractional concentration" employed by Harkins (*J. Amer. Chem. Soc.*, 1911, **33**, 1851). In Figs. 1 and 2, the values of s/s_0 are plotted against the values of c/s_0, for the addition respectively of uni-bivalent and bi-bivalent salt. For comparison, a typical curve for the system uni-univalent salt + univalent common ion (silver propionate + sodium propionate, Arrhenius, *Z. physikal. Chem.*, 1899, **31**, 225) is also shown (dotted curve).

The curves all lie considerably above the curve for the uni-univalent salt, and for any one saturating salt the curve of Fig. 2 lies above that of Fig. 1. Moreover, for one type of added salt, the curves all lie in the order of the solubility of the saturating salt in pure water, the curve taking a higher position the greater the solubility; this order was found to hold by Harkins (*loc. cit.*) for the salts investigated by him. The lowering effects of calcium and magnesium succinates on the solubility of barium succinate are almost equal, the crosses on curve 2 (Fig. 2) denoting addition of calcium succinate.

Noyes (*J. Amer. Chem. Soc.*, 1924, **46**, 1080, 1098), in his critical presentation of the interionic attraction theory of ionised solutes as put forward by Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 742) and by Debye and Hückel (*Physikal. Z.*, 1923, **24**, 185), uses some of the existing data on the solubility of salts in salt solutions in order to test the validity of the theory. He finds that the solubility effects should be given by an equation, which takes the follow-

FIG. 1.   FIG. 2.

1 CaSucc + Na₂Succ.
2 SrMal + SrCl₂
3 Sr Succ + Na₂Succ.
4 BaSucc + Na₂Succ.

1 Ca.Succ + MgSucc.
2 BaSucc + MgSucc. ⊙
  „   + Ca.Succ. +
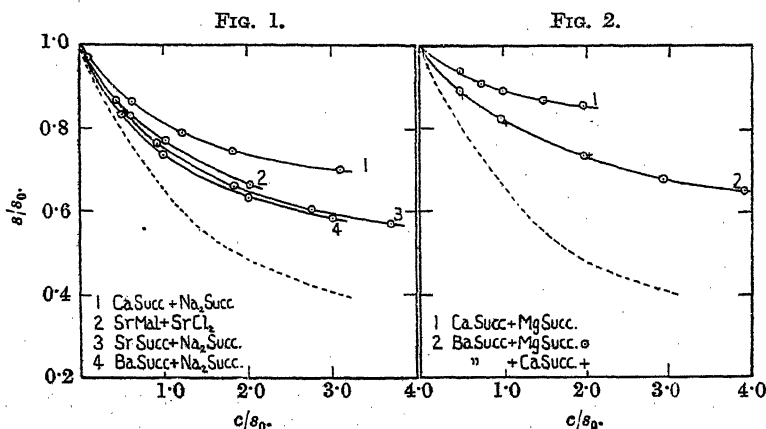
ing form for bi-bivalent saturating salts, s_0, s, and c being the concentration terms hitherto employed in this paper,

$$\tfrac{1}{8} \log \frac{s(s + c)}{s_0{}^2} = \alpha(\sqrt{\Sigma c' \nu^2} - \sqrt{8 s_0}),$$

where α has the theoretical value of 0·357 for dilute solutions at 25°. $\Sigma c' \nu^2$ denotes the summation of ion concentration (c') × square of valence of ion (ν^2) for all the ions present, half this quantity representing the " ionic strength " as defined by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1140). In Table II are shown the values of the coefficient for the two least soluble salts, barium succinate and strontium succinate, calculated from the solubility data in Table I. The values for the system calcium sulphate + magnesium sulphate calculated from the data quoted in Noyes's paper are also shown.

The values in each column are arranged in order of increasing total salt concentration, and it will be seen that in this order α in most cases decreases, reaching a value of about 0·15 at ionic strengths between 0·2 and 0·45 molar. The data for the case of calcium succinate as saturating salt, a salt about four times as soluble as any of the saturating salts in Table II, give even smaller values of α, about 0·09 in the most concentrated solutions. Whilst

TABLE II.

Values of a.

"Ionic strength." $\frac{1}{2}\Sigma c'\nu^2$.	Ba succ. + Mg succ. $s_0=0.01570$.	Ba succ. + Ca succ. $s_0=0.01570$.	Ba succ. + Na succ. $s_0=0.01570$.	Sr succ. + Na succ. $s_0=0.02013$.	CaSO$_4$ + MgSO$_4$. $s_0=0.01517$.
0.08 to 0.20	0.181 0.177 0.164	0.173 0.172 0.164	0.165 0.171 0.168	0.186 0.166 0.158	0.201 0.196 0.181
0.20 to 0.45	0.153 0.147		0.165	0.152 0.145	0.169 0.150

the values of α in the first three rows of the table are constant to within about 10%, they are still somewhat smaller than the value 0·238, which Noyes finds to satisfy the experimental facts up to ionic strengths of $0.1M$ in the case of the three salts of higher valence type quoted by him. The differences in the values of α from one another are greater than those which could be due to experimental error in the value of the solubility. An error in the latter as great as 1% (the actual maximum error was about 0·5%) makes a difference of about 5% in the values of α.

Although α increases with decreasing salt concentration, extrapolation from the graph obtained by plotting concentration against the corresponding values of α does not show any tendency for α to reach a value as high as 0·357, even at very small concentrations. In order, therefore, to obtain data at much smaller concentrations than those employed so far in this paper, some experiments were carried out on the solubility of barium and magnesium oxalates in presence of barium chloride and magnesium sulphate respectively. It was hoped that the results of these experiments would give an indication of the value of the " constant " α in Noyes's equation at these much smaller concentrations (about 0·003 to 0·0006 weight-molar), for which the equation ought to hold more closely than in the cases already dealt with. The solubility was determined in each case by titration of the amount of oxalate present in about 200 g. of solution with carefully standardised permanganate solution of such a strength that from 30—60 c.c. were used up in the titration.

From these results, no consistent value for α was obtained in the case of barium oxalate. At small concentrations corresponding to the solubility of barium oxalate, a small error in the experimentally obtained value of the solubility becomes highly magnified in the calculation of α, which may consequently vary enormously. With the more soluble magnesium salt, the influence of an experimental error is not so marked, an error of 1·0% in the solubility causing an error of about 5% in the value of α. The results obtained with magnesium oxalate ($s_0 = 0.00307$) in presence of magnesium

sulphate are as follow, the values of α being calculated from Noyes's equation :

$s.$	$c.$	$a.$
0·00235	0·00272	0·285
0·00215	0·00491	0·320

These values of α are much nearer the theoretical value of 0·357, and the agreement between the two values is fairly good, as the experimental error here corresponded with an error of about 5% in the value of α.

Summary.

(1) The solubility has been determined at 25° of some bi-bivalent salts, *viz.*, succinates and malonates of calcium, strontium, and barium, in pure water and in solutions containing varying concentrations of a common ion. Curves are given which show that the solubility is in every case greater than would be predicted by the solubility product rule, and that the divergence is more marked the greater the solubility of the salt considered, and greater for an added bi-bivalent salt than for an added uni-bivalent salt.

(2) The solubility data have been examined from the point of view of the interionic attraction theory of ionised solutes as developed by Debye and Hückel and especially, from the solubility point of view, by Noyes. The results obtained in this paper are in good qualitative agreement with this theory and, in the case of the very sparingly soluble magnesium oxalate, a fair quantitative agreement is obtained.

X.—*Organic Compounds of Arsenic. Part II. Derivatives of the Arsenic Analogue of Carbazole.*

By JOHN ALFRED AESCHLIMANN, NORMAN DEMPSTER LEES, NIAL PATRICK MCCLELAND, and GEORGE NORMAN NICKLIN.

TURNER and BURY have shown (J., 1923, **123**, 2489) that the closure of five-membered arsenic rings of the type *As*-methyl-dihydroarsindole can be accomplished without difficulty, and two of us have found (J., 1924, **125**, 2025) that the same applies to certain five-membered rings containing three atoms of carbon, one atom of oxygen, and one of arsenic.

It is now shown that the five-membered arsenic ring of analogues of carbazole can be closed with similar ease and it is hoped to give in a future communication an account of the formation of arsenic analogues of indoxyl and related substances.

o-Aminodiphenyl, subjected to the Bart reaction, yields *diphenylyl-o-arsinic acid* (I), and this is converted by warm concentrated sulphuric acid into oo′-*diphenylylenearsinic acid* (II).
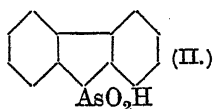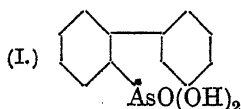
Similarly, diphenylyl-o-arsenious chloride, on distillation in a vacuum, is converted into oo′-*diphenylylenearsenious chloride*. Various other derivatives of oo′-diphenylylenearsine have been prepared, but the parent substance could not be isolated owing to the readiness with which it is oxidised in the air.

The derivatives are all beautifully crystalline, colourless with the exception of the *iodide*, and non-fluorescent. The melting point is usually about 100° higher than that of the corresponding diphenyl derivative.

E X P E R I M E N T A L.

o-*Aminodiphenyl.*—Hirsch's method for the preparation of this base (*Ber.*, 1892, 25, 1973) was modified in that the diazoamino-benzene was prepared as a separate operation, whereby the volume of solvent was much reduced and the tedious drying over potash obviated. Further, since it was not necessary to isolate *p*-amino-diphenyl, the separation of the required base from the other products of the reaction was considerably simplified.

Diazoaminobenzene (150 g.) is covered with 400 g. of aniline (both thoroughly dry) in a large distilling flask, and heated until (at about 150°) a brisk evolution of nitrogen begins; after which the reaction should proceed smoothly to completion, the temperature slowly rising to 180°. Care is necessary not to overheat the mixture, as the reaction may then get out of control. After removal of the aniline, the residue is distilled to about 250° (20 mm.) or until the distillate is very much coloured. The oily distillate is treated with warm dilute sulphuric acid (60 g. in 1 litre for 100 g. of the oil), the residue (diphenylamine and *p*-aminodiphenyl sulphate) removed, and the solution concentrated, almost to dryness. The sulphate of *o*-aminodiphenyl crystallises, while most of the aminoazobenzene sulphate remains in the mother-liquors. The base is obtained from the sulphate in the usual manner and distilled in a vacuum (yield about 25 g.). For further

purification, crystallisation of the hydrochloride from concentrated hydrochloric acid by cooling a saturated solution to $-10°$ is recommended.

Diphenylyl-o-*arsinic Acid* (I).—Sodium arsenite is coupled with diazotised o-aminodiphenyl in alkaline solution at 50—60° in presence of a cupric salt. The acid crystallises from boiling water in bristle-like needles, m. p. 205°. Yield about 60% (Found : C = 51·7; H = 4·1. $C_{12}H_9O_3As$ requires C = 51·8; H = 4·0%).

Diphenylyl-o-*arsenious chloride*, obtained by the reduction of the above dissolved in warm concentrated hydrochloric acid, by sulphur dioxide in presence of an iodide, is a heavy oil, soluble in chloroform, insoluble in water. On distillation in a vacuum, it loses hydrogen chloride and yields oo'-diphenylylenearsenious chloride.

Diphenylyl-o-*arsenious oxide*, obtained by the action of alcoholic potash on the above, is an amorphous substance with no definite melting point.

oo'-*Diphenylylenearsinic Acid* (II).—A solution of diphenylyl-o-arsinic acid in concentrated sulphuric acid is warmed on the water-bath for a few minutes and poured into water.

oo'-*Diphenylylenearsinic acid* can be crystallised from very much boiling water, m. p. 290° (Found : C = 55·2; H = 3·5. $C_{12}H_9O_2As$ requires C = 55·4; H = 3·5%).

oo'-*Diphenylylenearsenious Chloride*.—Diphenylylenearsinic acid is suspended in concentrated hydrochloric acid, an equal volume of chloroform added, and sulphur dioxide and hydrogen chloride are passed in through a wide delivery tube opening under the surface of the chloroform. After some minutes, a little potassium iodide is added and the reduction carried on under reflux on a water-bath, when diphenylylenearsenious chloride passes into the chloroform layer. It is recrystallised from benzene.

oo'-*Diphenylylenearsenious chloride* crystallises with remarkable readiness, in colourless plates, m. p. 161°, b. p. about 230°/25 mm., readily soluble in chloroform or carbon tetrachloride, less soluble in benzene or alcohol (Found : Cl = 13·3. $C_{12}H_8ClAs$ requires Cl = 13·5%).

Diphenylylenearsenious Iodide.—A suspension of diphenylylene-arsinic acid in 10% sulphuric acid is saturated with sulphur dioxide at 60°, and a strong solution of potassium iodide added. After further reduction for an hour, the solid is removed and taken up in benzene; the solution is dried, filtered, and evaporated to small bulk. The *iodide* is then precipitated with alcohol. It forms very beautiful, golden plates, m. p. 166°, soluble in benzene or chloroform, practically insoluble in alcohol.

oo'-*Diphenylylenearsenious oxide*, obtained by the action of warm alcoholic potash on the chloride, or of concentrated aqueous ammonia on the iodide, forms white crystals, m. p. 178°, readily soluble in organic solvents (Found : C = 61·4; H = 3·4. $C_{24}H_{16}OAs_2$ requires C = 61·3; H = 3·4%). From alcohol it crystallises in needles, m. p. 117°, containing alcohol of crystallisation.

oo'-*Diphenylylenearsenious Cyanide.*—The oxide is dissolved in the least quantity of cold chloroform or of absolute alcohol and treated with anhydrous hydrocyanic acid ($\frac{1}{3}$ vol.). The product is crystallised from warm absolute alcohol to which a little anhydrous hydrocyanic acid is added as the temperature falls. The cyanide forms long, silky needles, m. p. 178° (like the oxide), soluble in the usual organic solvents (Found : C = 61·5; H = 3·1; N = 5·5. $C_{13}H_8NAs$ requires C = 61·7; H = 3·2; N = 5·6%).

Attempts to Prepare oo'-*Diphenylylenearsine.*—To diphenylylene-arsinic acid mixed with amalgamated zinc, hydrochloric acid was added and the whole covered with a layer of ether, the air in the flask being replaced by hydrogen. After some days, the clear ethereal layer became cloudy after a short exposure to the air, indicating the presence of the arsine, which could not, however, be isolated. The solution was colourless and non-fluorescent.

Diphenylylenemethylarsine.—By the action of magnesium methyl iodide on diphenylylenearsenious iodide suspended in ether, the yellow colour of the latter was discharged. On working up the product in the usual way, a substance was obtained which crystallised from alcohol in large, transparent prisms, m. p. 46°. It was probably the arsine required, but analytical results were not very satisfactory even after several crystallisations (Found : C = 65·0, 65·1; H = 4·4, 4·4. $C_{13}H_{11}As$ requires C = 64·5; H = 4·5%). The substance had a pleasant orange-like smell.

Diphenylylenedimethylarsonium iodide, obtained by heating the above with methyl iodide, forms needles, m. p. 190°, soluble in alcohol, insoluble in ether. The iodine is ionic and may be determined by titration with silver nitrate (Found : I = 33·3. $C_{14}H_{14}IAs$ requires I = 33·1%). Methylcarbazole does not combine with methyl iodide.

XI.—*Synthesis of Arachidic Acid and some Long-chain Compounds.*

By NEIL K. ADAM and JOSEPH W. W. DYER.

THE melting points of methyl and ethyl arachidates, and eicosyl alcohol, recorded in the literature are several degrees higher than those proper to compounds of their length of chain in the respective series. The regular rise of melting point in the even series of long-chain compounds is more than a mere empirical relationship, since one of us showed (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 528) that from this rise, and other regularities, a crystal structure could be predicted which has since been shown by X-ray methods to be correct (Muller and Shearer, J., 1923, **123**, 2043, 3152, 3156). Having synthesised arachidic acid from stearic acid by means of malonic ester, we find that the melting points of these derivatives are as follows. Ethyl arachidate, 41·5° to 42·5°; methyl arachidate, 46° to 47°; eicosyl alcohol, 65° to 65·5°. Previously recorded values are; ethyl ester, 49° (Schweizer, *Arch. Pharm.*, 1884, **222**, 768), 50° (Gossmann, *Annalen*, 1854, **89**, 10); methyl ester, 54·5° (Haller, *Compt. rend.*, 1907, **144**, 598); 53° (Schweizer, *loc. cit.*); alcohol, 71° (Haller, *loc. cit.*). Our values are nearly the mean between the melting points of the compounds in the 18- and 22-carbon series; the older ones are in some cases higher than those in the 22-carbon series. The melting point of arachidic acid itself is 75°, in agreement with previous results and with the position in the series.

The synthesis from ethyl stearate gave a 41% overall yield of pure arachidic acid, and appears to be much the easiest method of obtaining compounds of the C_{20} series pure.

We record also a modification of the Bouveault and Blanc reduction, convenient for long-chain compounds; and new preparations of eicosyl acetate, eicosylamine hydrochloride, eicosylcarbamide, acetohexadecyl- and aceto-octadecyl-amides, dioctadecylmalonic acid, and dioctadecylacetic acid.

EXPERIMENTAL.

Reduction of Long-chain Esters with Sodium and Alcohol.—The higher ethyl esters are troublesome in the ordinary process owing to their small solubility in alcohol. Addition of a large bulk of light petroleum, and substitution of wire or dust for the lumps of sodium, give good yields of the alcohol.

Octadecyl Alcohol.—Well-dried ethyl stearate (150 g.), dissolved in 1200 c.c. of light petroleum and 150 c.c. of absolute alcohol,

was added during $\frac{1}{2}$ hour to sodium wire (72 g.) covered with a little light petroleum to prevent oxidation, at about 80°; heating was continued for 6 hours with occasional shaking. The solvents were distilled off, the residual solid was treated with hot brine, and, after filtration, the product was dried and extracted with ether. The ether was evaporated, and the residue distilled at 12 mm. pressure (yield 68·5%).

For quantities less than 20 g. of ester, the process was modified by using sodium pulverised under xylene, and gave similar yields.

Eicosyl alcohol, from 4·82 g. of ethyl arachidate, was obtained in 70% yield. It was not distilled, but crystallised to constant m. p. (65—65·5°) from 90% alcohol.

Eicosyl acetate, prepared by dissolving the alcohol in glacial acetic acid and passing hydrogen chloride, was crystallised from aqueous acetone; m. p. 39·5—40·5° (Found : C = 77·54; H = 13·04. Calc., C = 77·49; H = 13·05%).

Preparation of Iodides and of Derivatives of Malonic Acid.— Passing hydrogen iodide into the molten alcohols (see Krafft, *Ber.*, 1886, **19**, 2984) gave quantitative yields of the iodides, the gas being practically completely absorbed until the reaction was complete.

The iodide, washed in ethereal solution, was heated with the theoretical amount of sodium and ethyl malonate, in absolute alcohol. The mixture became neutral and gave ethyl mono-octadecyl-malonate after 2 hours' boiling and standing over-night. Hydrolysis with strong aqueous potash was nearly instantaneous. The calcium salt was prepared and extracted with alcohol and ether, and the malonic acid liberated in 70% yield (calculated on the iodide used) by rubbing the purified calcium salt with hydrochloric acid in presence of a little ether, which promotes wetting.

Ethyl dioctadecylmalonate could not be prepared in one operation, but was obtained by heating, for 6 hours, 12·2 g. of the crude mono-octadecylmalonic ester with 0·682 g. of sodium, 11·5 g. of octadecyl iodide, and 30 c.c. of absolute alcohol, a little dry ether being added to obtain a homogeneous liquid. After 48 hours' standing, the mixture was neutral. The ester was hydrolysed by heating on the water-bath with alcoholic potash for 10 hours; the *dioctadecyl-malonic acid* was purified by means of the calcium salt, as before, and recrystallisation from glacial acetic acid. M. p. 93·5—94° [Found : C = 76·88; H = 12·33. $(C_{18}H_{37})_2C(CO_2H)_2$ requires C = 76·89; H = 12·57%].

Dioctadecylacetic Acid.—Heating dioctadecylmalonic acid at 160° left a residue, m. p. 80—82°; this was raised to 81—82° by crystallisation from acetic acid [Found : C = 80·63; H = 13·59. $(C_{18}H_{37})_2CH·CO_2H$ requires C = 80·76; H = 13·56%].

Guthzeit (*Annalen*, 1881, **206**, 362) describes dicetylmalonic acid (m. p. 86—87°) and dicetylacetic acid (m. p. 69—70°); his work has been criticised by Krafft, since the cetyl alcohol used was not pure.   If the crystal structure of these compounds is generally the same as that of the simple fatty acids, with the long chains packed side by side and the molecules arranged in pairs of layers, the polar groups of one layer of the pair being next to the polar groups of the other layer, we should expect the difference of two carbon atoms to make a difference of about 3° in the m. p.'s of the dialkylmalonic acids and of about 6° in those of the dialkylacetic acids, which would indicate for the pure dihexadecylmalonic acid m. p. about 91°, and for dihexadecylacetic acid, m. p. about 75°.

Arachidic Acid and its Esters.—The arachidic acid obtained by heating the monooctadecylmalonic acid distilled at 203—205° (uncorr.)/1 mm., and crystallised in leaflets from light petroleum; m. p. 75—75·5°.   Titration in alcoholic solution with soda gave the molecular weight 313 (theory 312·3) (Found : C = 76·73; H = 12·96.   Calc., C = 76·85; H = 12·90%).

Methyl arachidate was prepared by passing hydrogen chloride into a solution of the acid in pure methyl alcohol, and recrystallising from alcohol.   M. p. unchanged on recrystallisation, 46—47° (Found : C = 76·96; H = 12·98.   Calc., C = 76·85; H = 12·90%).

Ethyl arachidate, prepared similarly, and crystallised to constant melting point, melted at 41·5—42·5°.

Preparation of Long-chain Amides.—Fileti and Ponzio's method of adding a solution of the acid chloride in ether to aqueous ammonia (*Gazzetta*, 1893, **23**, 391) gives much better results than methods in which the ether is omitted.   These frequently give a product with a melting point 10 degrees too low, which probably consists largely of ammonium salt.   Using ether as solvent for the chloride, large quantities of the amide may be prepared, the chloride being added very rapidly, and the product is practically pure without crystallisation.   The ether is almost entirely driven off by the heat of reaction, and appears to act as a very efficient cooling agent. The aqueous ammonia may be at room temperature.

Arachidamide, m. p. 109°, and the nitrile, m. p. 49·5°, were prepared by the usual methods from the acid.

Eicosylamine hydrochloride was prepared by a modification of Krafft's method (*Ber.*, 1889, **22**, 812) for hexadecylamine.   The nitrile (9·7 g.) in 150 c.c. of absolute alcohol was boiled under reflux, 15 g. of sodium being added during 1 hour.   The mixture was poured warm into dilute hydrochloric acid, heated with 250 c.c. of absolute alcohol, filtered from any inorganic chlorides, diluted to about 85% alcohol, and cooled.   The solution deposited 8·5 g.

of pure eicosylamine hydrochloride, 1 g. more being obtained on concentrating the mother-liquors. For analysis, the chlorine was precipitated with alcoholic silver nitrate (Found: Cl = 10·66. $C_{20}H_{43}N$,HCl requires Cl = 10·64%).

Eicosylcarbamide was easily prepared by evaporating the preceding compound to dryness with excess of potassium cyanate and recrystallising from alcohol. M. p. 111·5° (corr.) (Found: C = 73·98; H = 13·13; N = 8·25. $C_{20}H_{41}$·NH·CO·NH$_2$ requires C = 74·00; H = 13·04; N = 8·25%).

Monomolecular films of all the compounds of the C_{20} series were examined according to the methods described in previous papers (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 452, 516) and were found to have the properties expected for their respective series and the C_{20} chain, within experimental error; a fact which confirms their identity.

Aceto-octadecylamide.—Octadecylamine hydrochloride (1·4 g.), prepared in the same manner as eicosylamine hydrochloride, was distilled with quicklime, the distillate warmed with acetic anhydride a few minutes, and the product crystallised from acetic acid with the aid of charcoal; m. p., unchanged by further crystallisation, 79·5—80° (yield 66%). The action of acetyl chloride on the amine gave a very poor yield of the desired substance (Found: C = 77·23; H = 13·4; N = 4·75. $C_{18}H_{37}$·NH·CO·CH$_3$ requires C = 77·09; H = 13·2; N = 4·50%).

Acetohexadecylamide was similarly prepared, and crystallised from acetic acid and acetone to constant melting point (Found: C = 76·46; H = 13·35. $C_{16}H_{33}$·NH·CO·CH$_3$ requires C = 76·69; H = 13·22%). In the monomolecular films, the acetamides showed a characteristic behaviour, described in another paper, which indicated that the compounds were members of the same homologous series, and differed by two CH$_2$ groups.

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XII.—*The Adsorption of Catalytically Poisonous Metals by Platinum. Part I. The Adsorption of Lead and Mercury.*

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MEASUREMENTS have been described (J., 1921, **119**, 225; 1922, **121**, 1760) relating to the inhibitive influence of salts of certain metals on the hydrogenation of unsaturated substances and on the decomposition of hydrogen peroxide. In each case it appeared

probable on first principles that adsorption of the metallic salt, or rather of the catalytically poisonous ion, by the catalyst took place ; but, since the degree of adsorption was unknown, the inhibitive effect of the poison, measured by the depression in the activity of the catalyst, could only be plotted against the initial bulk concentration of the inhibitant in the reacting system, in place of— as would have been more logical—its actual concentration on the surface of the catalyst itself.   Accordingly, the present work was carried out with the object of obtaining data relative to the variation of this adsorbed concentration with the bulk concentration of the inhibitant.   The present paper deals with the adsorption of lead and of mercury by finely divided platinum.

<div align="center">Ε Χ Ρ Ε R Ι Μ Ε Ν Τ Α L.</div>

An aqueous suspension of platinic oxide was reduced with hydrogen, the precipitated metal washed several times with hot distilled water, and ground thoroughly in an agate mortar in presence of a little water.   This method of preparing the platinum was found preferable to the reduction of a platinum salt with formaldehyde or other reducing agent on account of the difficulty, in such cases, of freeing the preparation from adsorbed impurities.

In carrying out each adsorption experiment, 1 c.c. of a stock suspension of platinum, containing 4·48 mg. of platinum per c.c., was added to a system containing a known quantity of a lead or mercury salt dissolved in 9 c.c. of water, the mixture was thoroughly agitated, kept over-night at 20°, and an appropriate portion of the clear liquid taken for analysis.

The concentration of lead or mercury salt remaining unadsorbed was determined by observing the toxic effect of a known fraction of the solution on the activity of a standard catalyst for the decomposition of hydrogen peroxide, for which reaction the inhibitive effect of various known concentrations of the lead and mercury salts in question had previously been mapped for the catalysts employed.   It was thus possible to estimate with considerable accuracy small fractions of a milligram of lead or of mercury.

Adsorption of Lead.—An aqueous solution of lead acetate, usually containing 0·1 mg. of lead per c.c., was employed; for certain experiments, solutions of one-tenth and ten times this strength, respectively, were used.   Preliminary experiments with potassium acetate showed that the acetate ion is, at any rate in the concentrations employed, without appreciable toxic action on platinum for the decomposition of hydrogen peroxide.

The result of a series of adsorption experiments, in each case with 4·48 mg. of platinum, is shown graphically in Fig. 1.   It will

be seen, on plotting the weight of lead adsorbed against its initial concentration, that a linear relationship exists between these two quantities up to a stage at which the platinum surface apparently approaches saturation; and further adsorption, from this stage onwards, takes place only to a slight degree on increasing the initial bulk concentration of the lead salt.   The two graphs in the figure were obtained by plotting the weight of lead adsorbed per gram of platinum, first, against the initial bulk concentration and, secondly, against the final bulk concentration of the unadsorbed lead in the system.   This result is analogous to those obtained by Euler and Hedelius (*Arkiv Kem.*, 1920, **7**, 31) for the adsorption of a silver

FIG. 1.

Bulk concentration of lead.   Mg. in 10 c.c.
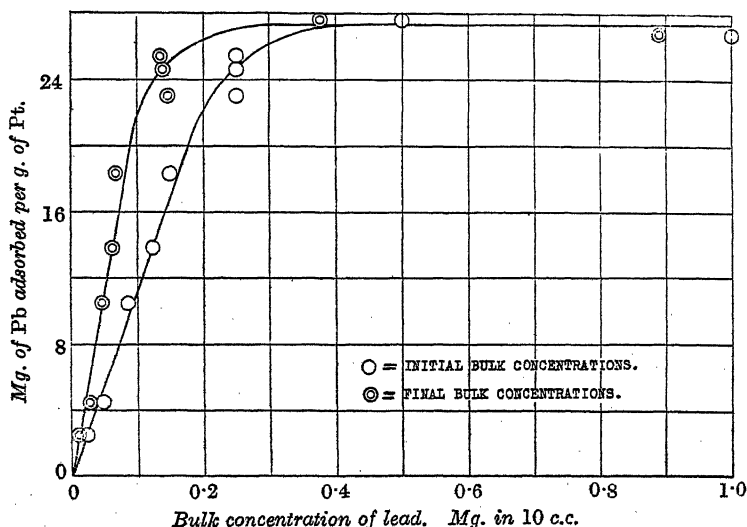
salt by silver and gold, for which also an initially linear adsorption graph was obtained.

Adsorption of Mercury.—A dilute solution of mercuric chloride was employed, the other conditions being similar to those adopted for lead.

Fig. 2 gives the results of a series of adsorption experiments, carried out, as before, with 4·48 mg. of finely divided platinum. For initial concentrations of mercury below that corresponding with the saturation of the platinum, the adsorption of mercury is practically complete; and the very small concentration of mercury remaining after adsorption could be estimated with the required degree of accuracy only by virtue of the method of analysis employed (see above).

D* 2

The linear nature of the adsorption graph for mercury, and the abrupt break in this graph immediately before the saturation point, are very striking.

The form of the adsorption graph both for lead and for mercury, on platinum, may be compared with that of the poisoning curve. It has previously been shown (*loc. cit.*) that the decrease in the activity of a platinum catalyst, caused by a poison such as lead or mercury, is, for by far the greater portion of the poisoning curve, a linear function of the initial bulk concentration of the poison in the system. It has now been shown that the mass of such a poison, *e.g.*, lead, actually adsorbed by platinum—*i.e.*, the concentration of the lead on the surface of the platinum—is also a linear function of this initial bulk concentration of the lead in the system. From

Fig. 2.

Bulk concentration of mercury. Mg. in 10 c.c.
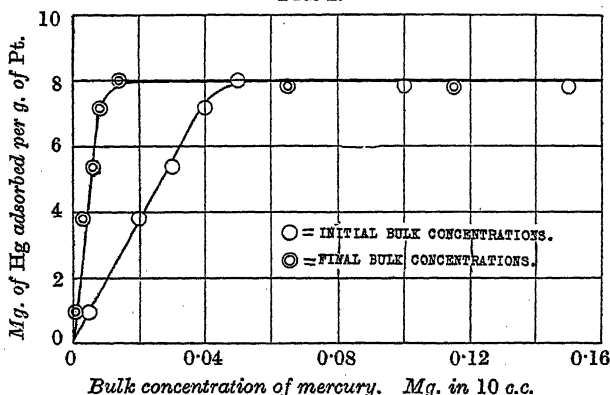
this it follows that the activity of the catalyst in the presence of such a poison is, at any rate for this first stage, a linear function of the actual concentration of the lead on the surface of the catalyst.

This result was to be expected on theoretical grounds, since the free valency forces on the surface lattice of the platinum will, if they are saturated by a difficultly evaporable poison, such as lead, no longer be free for the adsorption of, or association with, a potentially reactive system, it being presumed that catalysis normally takes place by reason of such association. Therefore, since each atom of lead thus obstructively adsorbed will cause a given number (one or more) of such valency bonds to become no longer active for normal catalysis, the poisoning of this catalytic surface should be a linear function of the concentration of the poison on the surface, a result which has just been obtained experimentally.

From Fig. 1 it is seen that the linear relationship between the concentration of the lead on the catalyst and its bulk concentration

in the solution ceases, as is necessarily the case, in the region border-
ing on the saturation of the surface of the platinum by the lead,
in which region the initially linear adsorption graph becomes more
or less abruptly converted into a line parallel with the bulk concen-
tration axis and denoting saturation.

In the poisoning graphs previously obtained for such cases, the
initial linear portion—during which the activity of the catalyst
is a linear function of the initial bulk concentration of the poison
in the system—is also followed, in a very similar way, by a break,
followed in turn by a far less steep portion, which, like the adsorption
curve, becomes approximately parallel with the bulk concentration
axis.   It appears of great interest to ascertain whether the break
in the poisoning graph, obtained by plotting activity against bulk
concentration of the poison, occurs at the region of incipient satur-
ation.   If this is the case, then the activity of the catalyst would
seem to be linearly proportional to the actual concentration of
poison on the surface of the catalyst, not only during the major
portion of the poisoning graph, but also up to the complete extinction
of catalytic activity.   It is hoped to discuss this point more fully
in a later paper.

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XIII.—*The Explosion of Acetylene and Nitrogen. Part IV. Spectra of Explosions of Gases containing Hydrogen, Carbon, Nitrogen, and Oxygen.*

By William Edward Garner and Sidney Walter Saunders.

The origin of the Swan and cyanogen band spectra has frequently
been discussed, and although the former is usually ascribed to free
carbon (Watts, *Phil. Mag.*, 1914, [vi], **28**, 117) and the latter to
carbon and nitrogen, opinion is not unanimous on these questions.
Before 1914, it was believed that the cyanogen bands were due to
carbon and nitrogen, but Grotrian and Runge (*Physikal. Z.*, 1914,
15, 545) reopened the discussion on the origin of this spectrum,
and concluded, as a result of their experiments with the electric
arc, that the so-called cyanogen spectrum was due to nitrogen
alone.   This view seems to have been widely accepted, although
neither Barratt (*Proc. Roy. Soc.*, 1920, [*A*], **98**, 40), who experi-
mented with flames, nor Hemsalech (*Phil. Mag.*, 1920, [vi], **39**,
241), nor Holst and Oosterhuis (*K. Acad. Amsterdam Proc. Sci.*,
1921, **23**, 1, 727), who suppressed the cyanogen bands by immersing

their nitrogen and argon discharge tubes in liquid oxygen, and so freezing out the cyanogen, have confirmed it. The results obtained in this paper also indicate that the presence of both carbon and nitrogen is essential for the production of the " cyanogen " spectrum.*

It has been found that the nature of the spectrum emitted during explosions of acetylene in oxygen and nitrogen is very largely dependent on the ratio of gram-atoms of carbon to oxygen in the mixture. With low percentages of oxygen, where large quantities of carbon are deposited during the explosion, a continuous spectrum only is obtained. The carbon, being an almost perfect black body, acts as a screen cutting off the radiation emitted from the molecules activated during the explosion. As the ratio of oxygen to acetylene approaches unity, the Swan, CH, and cyanogen bands, and metallic absorption and emission lines appear on the background formed by the continuous spectrum, which simultaneously diminishes in intensity. These band spectra persist into the region where oxygen>carbon, but gradually fade away as the oxygen percentage is increased, until, finally, with a still larger proportion of oxygen, only the line emission and absorption spectrum of the metallic impurities are present.

The Swan and cyanogen spectra appear and disappear together as the oxygen percentage increases. Their disappearance occurs approximately at the concentrations found previously (J., 1924, 125, 1634) for the disappearance of free carbon and hydrocyanic acid from the final products of the explosion, viz., when the ratio of oxygen to carbon becomes unity. Thus the presence of free carbon in the products of the explosion is essential not only for the production of hydrocyanic acid but also for both the Swan and the cyanogen spectra.

The Swan and cyanogen spectra persist into the region where oxygen is in excess (up to $C : O = 0.956$ for mixtures of C_2H_2 and O_2, and $C : O = 0.968$ for mixtures of O_2, N_2, and C_2H_2), but this does not invalidate the above conclusion, for the spectrum of the explosion is a record of the radiation emitted throughout the whole of the explosive process and hence includes the radiation emitted before equilibrium is reached.

On the molecular collision view of the propagation of the explosion wave, undecomposed acetylene molecules immediately in front of the wave will be bombarded by swiftly moving molecules of carbon, hydrogen, oxygen, carbon monoxide, etc., from the explosion wave itself. An oxygen molecule, in collision with an acetylene mole-

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* Since this paper was written Freundlich and Hochheim (Z. Physik, 1924, 26, 102), in furnace experiments, have shown that elementary carbon is essential for the production of this spectrum.

cule, would be likely to give carbon monoxide but no free carbon, $C_2H_2 + O_2 \longrightarrow 2CO + H_2$, but any other molecule may bring about the change $C_2H_2 \longrightarrow 2C + H_2$. Thus even in the presence of excess of oxygen free carbon may be momentarily formed, and, if the average life of the carbon particles (C_2 possibly) before removal as carbon monoxide is long enough, the Swan spectrum may be emitted. This would explain our results (Table I).

The results of this investigation thus support the view that carbon is necessary for the production of the cyanogen spectrum. That nitrogen also is necessary is evident from the absence of the cyanogen spectrum in the spectra of explosions of acetylene and oxygen alone.

EXPERIMENTAL.

An examination has been made of the spectra from the following series of explosive mixtures : (a) pure acetylene, (b) acetylene and nitrogen, (c) acetylene and oxygen, (d) acetylene, oxygen, and nitrogen, (e) electrolytic gas, (f) carbon monoxide and oxygen, (g) coal gas and oxygen.

Apparatus.—A 2-litre phosphor-bronze bomb similar to that described by Wheeler (J., 1918, **113**, 855) was fitted with a cylindrical quartz window, 6 mm. in diameter and 8 mm. thick, placed opposite the collimator tube of a Hilger Constant Deviation Spectrometer.* Ignition of the gaseous mixture was usually accomplished by fusion of a thin iron wire placed across the terminals in the centre of the bomb. In some experiments, the position of firing of the mixture was changed and in others, the iron wire was replaced by platinum.

Preparation of the Gases.—The acetylene, from a cylinder containing the gas compressed in acetone, was washed with water, dried over phosphorus pentoxide, and stored over mercury. It was completely soluble in a solution of ammoniacal cuprous chloride. Oxygen and nitrogen were prepared as described elsewhere *(loc. cit.)*. Carbon monoxide, obtained by the action of sulphuric acid on sodium formate, was washed with sodium hydroxide and dried over phosphorus pentoxide. Electrolytic gas was prepared from baryta. The gases were introduced into an evacuated bomb, which had been previously washed out six times with oxygen. This repeated washing was necessary in order to ensure the absence of nitrogen in the first series of experiments. The composition of the gaseous mixture was determined by pressure measurements.

Measurement of Spectra.—Each photograph of the explosion spectrum was bracketed by photographs of a neon-helium lamp, the wave-lengths of the lines in this spectrum being known, and

* A few measurements were made with a quartz spectrometer.

the lines were measured by means of a travelling microscope.
The extreme errors of measurement were ± 1Å. for the band
spectra and 0·2 Å. for the metallic lines.

Results.

(a) *Acetylene and Oxygen.*—With pure acetylene, and also
acetylene and oxygen mixtures up to 41% of oxygen, a perfectly
continuous spectrum was obtained (Table I). With 100% acetyl-
ene, the spectrum was rather more brilliant in the red than is the
case with the mixture containing 41% of oxygen. The effect of
the addition of oxygen on the position of maximum light intensity
is to shift this maximum slightly towards the blue end of the spectrum,
this being in agreement with Wien's displacement law.

TABLE I.

Oxygen and Acetylene. P = 1 atm.

% O_2.	% C_2H_2.	% C_2H_2/% O_2.	Spectrum.
—	100·0 *	—	Continuous with no line or band spectra.
35·22	64·78	1·837	
41·10	58·90	1·433	
49·33	50·67	1·028	Swan and CH bands with faint metallic lines.
49·58	50·42	1·017	
49·69	50·31	1·013	
50·30	49·70	0·988	Swan and CH bands with metallic lines.
51·12	48·88	0·956	
53·14	46·86	0·882	Metallic lines only.
55·50	44·50	0·802†	
59·86	40·14	0·671	
62·91	37·09	0·590†	

* 3·2 atm.   † Platinum wire ignition.

As the ratio (column 3) approaches unity, the Swan, "the three,"
and the CH bands appear on the continuous spectrum. The bands
6191, 5635, 5165, 4737, 4382, 4371, 4365, and 4314 Å. were observed.
These bands first appear when the value, %C_2H_2/%O_2, is between
1·433 and 1·035; the exact value was not found.

It was anticipated that the Swan spectrum would disappear
when %C_2H_2/%O_2<1, since at the temperature of explosion,
ca. 3000°, the equilibrium constant for the reaction $C + H_2O =
CO + H_2$ is $K_p = P_{CO}P_{H_2}/P_{H_2O} = 10^5$, and hence practically no
free carbon can be present if the gaseous mixture attains equilibrium.

Since the Swan spectrum is considered as being due to free
carbon, it was expected that this, together with "the three"
and CH bands would disappear when the ratio %C_2H_2/%O_2 <1.
It was found, however, that these bands persisted even when the
acetylene–oxygen mixture had the ratio %C_2H_2/%O_2 = 0·956,
although they had all disappeared when the ratio became 0·882.

The cyanogen spectrum was not observed in this series of experiments.

(b) *Acetylene, Nitrogen, and Oxygen.*—When nitrogen was added until the mixture had the composition 82% C_2H_2, 18% N_2, and the mixture was fired under a pressure of about 3 atmospheres, several units per cent. of hydrocyanic acid were obtained and yet the spectrum was still continuous.   Since the amount of free carbon could not be reduced sufficiently by the addition of nitrogen alone to enable emission and absorption lines to be obtained, oxygen was added to the mixture until the ratio %C_2H_2/%O_2 was between 1·1 and 1.   This diminished the carbon sufficiently for the Swan, "the three," and the CH bands to be observed, and, in addition, the cyanogen bands, 4216 Å. and 3883 Å.   These all persisted when the ratio %C_2H_2/%O_2 = 0·968 (Table II).   Further addition

TABLE II.

Oxygen, Nitrogen, and Acetylene. $P = 1$ atm.

% O_2.	% C_2H_2.	% N_2.	% C_2H_2/% O_2.	Spectrum.
—	82·2	17·8	—	Continuous spectrum.
47·98	49·56	2·46	1·035	
40·72	41·81	17·47	1·026	
48·65	49·22	2·13	1·012	Swan, CH, cyanogen bands and
49·28	49·99	0·73	1·013	faint metallic lines.
39·58	40·06	20·36	1·012	
46·72	46·14	7·14	0·988	
45·97	45·28	8·55	0·985	Swan, CH, cyanogen bands and
39·96	39·11	20·93	0·977*	metallic lines.
42·92	41·49	15·60	0·968	
41·59	40·28	18·13	0·968	
43·13	39·45	17·42	0·915	
45·29	37·36	17·35	0·825	Metallic lines only.
51·66	39·79	8·55	0·770	
56·04	34·73	9·23	0·620	

* No band spectra.

of oxygen causes the disappearance of these spectra.   If Grotrian and Runge's contention be correct, that nitrogen will give rise to the "cyanogen" spectrum if no appreciable amount of oxygen be present, then the above-mentioned disappearance of this spectrum, when %C_2H_2/%O_2 = 0·915, is not easy to explain, for in such a mixture at the temperature of the explosion there can be but little free oxygen.*   The disappearance of this spectrum is understandable, however, if it be due to both carbon and nitrogen.

The nature of the spectrum is the same, whatever the position of the iron wire used for igniting the gases; placing the iron wire close to the side of the bomb or directly in front of the quartz window made no difference.

* Approximately 0·001 % of oxygen at 3000° abs.

The only lines present in the spectra of the explosions of hydrogen and oxygen, and carbon monoxide and oxygen, were those due to the metallic impurities present, *e.g.*, sodium, calcium, iron, etc. As would be expected on account of the lower temperature of these flames, the metallic lines were not so numerous as in the acetylene explosions.

Summary.

The spectra emitted during the explosion of mixtures of acetylene, nitrogen, and oxygen have been studied. The results indicate that the cyanogen spectrum is due to both carbon and nitrogen.

XIV.—*Reactions of Displacement in the Tropic Acid Group. Part I.*

By ALEX. MCKENZIE and ROBERT CAMPBELL STRATHERN.

THE proof of the constitution of α-aminohydratropic acid, $NH_2 \cdot CPhMe \cdot CO_2H$, was afforded by Tiemann and Köhler (*Ber.*, 1881, 14, 1980) by the synthesis from acetophenonecyanohydrin and alcoholic ammonia. McKenzie and Clough (J., 1912, 101, 390), in dealing with the Walden inversion, described the resolution of the r-acid into its optically active components.

The study of the isomeric β-acid, $NH_2 \cdot CH_2 \cdot CHPh \cdot CO_2H$, has not so far been advanced to the corresponding stage. For one reason, this acid has no particular interest with relationship to the Walden inversion, the amino-group not being directly attached to the asymmetric carbon atom. The identification of the acid has also been attended with some confusion. By the action of aqueous ammonia on β-bromohydratropic acid, Merling (*Annalen*, 1881, 209, 11) obtained crystals, m. p. 169—170° (compare also Fittig and Wurster, *ibid.*, 1879, 195, 158). Assuming that the reaction proceeded on the lines

$$CH_2Br \cdot CHPh \cdot CO_2H \longrightarrow NH_2 \cdot CH_2 \cdot CHPh \cdot CO_2H,$$
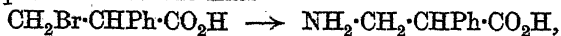
Merling concluded that he had to deal with β-aminohydratropic acid, and the analytical evidence supported this assumption.

Posner, however, in continuation of his work on the action of hydroxylamine on unsaturated acids, obtained from atropic acid an amino-acid which melted and decomposed at 234° (*Ber.*, 1903, **36**, 4315; *Annalen*, 1912, **389**, 109). All the evidence pointed to this substance being the true β-aminohydratropic acid. Since Posner (*Ber.*, 1905, **38**, 2316) had shown that the action of ammonia on β-bromo-β-phenylpropionic acid leads to the formation not of β-amino-β-phenylpropionic acid but of β-hydroxy-β-phenylpropionamide, he suggested that β-bromohydratropic acid might perhaps exhibit a similar behaviour, and that Merling's product was not the amino-acid at all, but was the isomeric tropamide.

The latter suggestion has been borne out. In the present paper it is shown that r-β-chlorohydratropic acid is converted into r-tropamide (m. p. 170—171°) by the action of aqueous ammonia. The amide was also prepared directly from ammonia and methyl *dl*-tropate; it has the same melting point, and it possesses the same properties as the compound described by Merling.

We have also examined the action of hydroxylamine on atropic acid, and find that Posner's β-amino-acid is not the sole product, and that the oxime of phenylacetaldehyde is also formed. It is, however, rather curious that the formation of tropic acid by the action of nitrous acid on the amino-acid proceeds in a somewhat irregular manner.

The preparation of l-β-chlorohydratropic acid is described, the resolution of the r-acid being effected in methyl-alcoholic solution with morphine as the resolving alkaloid. When hydrolysed, the l-acid, which has $[\alpha]_D - 122\cdot6°$ in benzene, gave a lævorotatory tropic acid with $[\alpha]_D - 58\cdot1°$ $(c = 2\cdot4348)$ in ethyl-alcoholic solution, whereas the value for the optically pure acid is $[\alpha]_D - 72\cdot5°$ $(c = 2\cdot578)$ in the same solvent (McKenzie and Wood, J., 1919, **115**, 828). Although the chlorine is not directly attached to the asymmetric carbon atom, some racemisation had apparently taken place during the substitution of the hydroxy-group for the chlorine.

In the light of recent work in a different field (McKenzie and Roger, J., 1924, **125**, 2148), the action of ammonia on the l-chloro-acid was of some interest, and we have therefore examined it for the purpose of finding if optical activity would persist in the transformation into the amide. Experiments showed that a lævorotatory tropamide did actually result. Under the conditions employed, the rotation of the product was less than that of the amide obtained by the direct action of ammonia on ethyl l-tropate. This formation of an optically active tropamide has led us to

conclude that a β-lactone is produced as an intermediate phase, thus :

$$l\text{-H}\underset{\overset{|}{\text{CO}_2\text{H}}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{CH}_2\text{Cl} \;\rightarrow\; l\text{-H}\underset{\overset{|}{\text{CO}_2\cdot\text{NH}_4}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{CH}_2\text{Cl} \;\rightarrow$$

$$l\text{-H}\underset{\overset{|}{\text{CO}\cdot\text{O}}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{CH}_2 \;\rightarrow\; l\text{-H}\underset{\overset{|}{\text{CO}\cdot\text{NH}_2.}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{CH}_2\cdot\text{OH}.$$
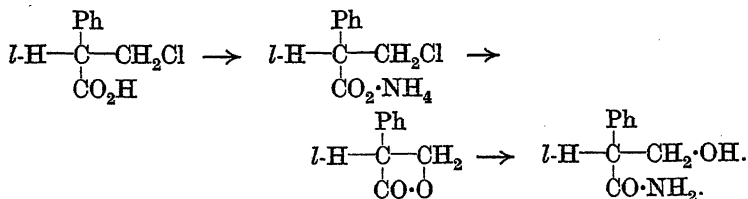
Although on those lines the actions do not occur by substitution of groups directly attached to the asymmetric carbon atom, some racemisation accompanied the change. This was not altogether unexpected, since in tropamide we have the phenyl, hydrogen, and carbonyl groups all directly attached to the asymmetric carbon atom, a system which, at any rate in the presence of alcoholic alkali, is particularly prone to racemisation under certain conditions (McKenzie and Smith, J., 1922, **121**, 1348).

In the field of optical activity, it has been shown by Holmberg (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 23, pp. 1-33, and earlier papers) that the formation of a β-lactone is a stage in the interconversion of d- and l-malic acids by the Walden inversion. Moreover, l-iodo-succinic acid, when treated with ammoniacal silver nitrate, gives a mixture of fumaric acid and d-β-malamic acid, the latter being formed by the action of ammonia on the d-malo-lactone (compare Walden and Lutz, *Ber.*, 1897, **30**, 2796; Lutz, *Ber.*, 1902, **35**, 2460, 4369; 1908, **41**, 841).

Reference has already been made to the fact that Posner obtained r-β-hydroxy-β-phenylpropionamide by the action of ammonia on r-β-bromo-β-phenylpropionic acid. It seems reasonable to suppose that this action proceeds on similar lines to that of ammonia on β-chlorohydratropic acid :

$$\text{H}\underset{\overset{|}{\text{CH}_2\cdot\text{CO}_2\text{H}}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{Br} \rightarrow \text{H}\underset{\overset{|}{\text{CH}_2\cdot\text{CO}_2\cdot\text{NH}_4}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{Br} \;\rightarrow\; \text{H}\underset{\overset{|}{\text{CH}_2\cdot\text{CO}}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{O} \rightarrow \text{H}\underset{\overset{|}{\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2.}}{\overset{\overset{\text{Ph}}{|}}{\text{—C—}}}\text{OH}$$
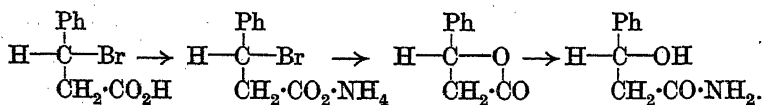
It will be observed that the β-lactone which is suggested as an intermediate phase is isomeric with the one postulated in the scheme with β-chlorohydratropic acid.

Arising from the results recorded in the present paper, and more especially from former work by one of us, it is desirable that Posner's observation should be extended to the optically active β-bromo-β-phenylpropionic acids so as to enable the following scheme to be completed :

$$\text{dextro-} \qquad\qquad\qquad\qquad \text{dextro-}$$
$$\text{C}_6\text{H}_5\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \quad \rightleftharpoons \quad \text{C}_6\text{H}_5\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{CH}_3$$
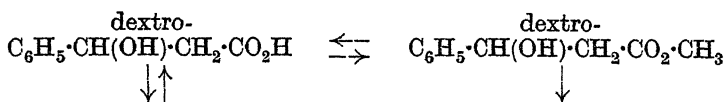
$$\text{lævo-C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \quad \text{dextro-C}_6\text{H}_5\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$$

(McKenzie and Humphries, J., 1910, **97**, 121; McKenzie and Martin, J., 1913, **103**, 112; McKenzie, Martin, and Rule, J., 1914, **105**, 1583; McKenzie and Smith, J., 1922, **121**, 1348). Owing to the announcement in the current number of the *Proceedings* (1924, p. 77) of a paper by Senter and Ward entitled "Studies on the Walden inversion. Part IX. The influence of the solvent on the sign of the product in the conversion of β-bromo-β-phenylpropionic acids to β-hydroxy-β-phenylpropionamides," we are not, meanwhile, investigating this matter further, so far as the action of ammonia on the optically active β-bromo-β-phenyl-propionic acids is concerned. At present, we are engaged on a further study of the action of nitrous acid on *r*-β-aminohydratropic acid, and also propose to undertake the resolution of this acid with the object of examining the resulting optically active acids.

<center>E X P E R I M E N T A L.</center>

Action of Hydroxylamine on Atropic Acid.—Posner (*Annalen*, 1912, **389**, 112) prepared *r*-β-aminohydratropic acid by heating atropic acid with an alcoholic solution of hydroxylamine for 1 hour. By analogy with his previous work (*Ber.*, 1905, **38**, 2316; compare also McKenzie and Tudhope, J., 1924, **125**, 923), it might be expected that the formation of the amino-acid would be accompanied by that of phenylacetaldoxime. This oxime was isolated as follows.

Hydroxylamine hydrochloride (25 g.) in water (25 c.c.) was added to a solution of sodium (8·5 g.) in ethyl alcohol (280 c.c.), and the precipitated sodium chloride removed. Atropic acid (25 g.), prepared by the dehydration of atrolactinic acid (McKenzie and Wood, *loc. cit.*), was added, and the solution boiled for 1½ hours. Ammonium carbonate was deposited in the condenser tube. After 3 days in the ice-chest, the amino-acid (8 g.) was collected; it was free from the hydroxylamino-acid, since it did not reduce either Fehling's solution or ammoniacal silver nitrate; it melted and decomposed at 222—224° (Posner gives 233°). An additional 0·5 g. was obtained by boiling the filtrate for 2¼ hours longer. After distillation of the bulk of the alcohol, an excess of water precipitated 8 g. of crude phenylacetaldoxime, which, crystallised from water several times, gave the pure substance in lustrous needles, m. p. 103—104° (Found: C = 70·9; H = 6·8. Calc., C = 71·1; H = 6·7%). Bouveault and Wahl (*Compt. rend.*, 1902, **134**, 1147) gave m. p. 103°.

r-β-Aminohydratropic acid is sparingly soluble in water, benzene, light petroleum, acetone, chloroform, carbon disulphide, and ether. Posner (*Ber.*, 1903, **36**, 4315) described this acid as α-amino-α-phenylpropionic acid (α-aminohydratropic acid); its solution in hydrochloric acid was acted on by nitrous acid to give an acid, m. p. 89—90°, which was supposed to be atrolactinic acid. Posner was, however, working with small quantities of material, and was misled by the erroneous data of other authors. In a subsequent paper (*Annalen, loc. cit.*), the correct constitution of the amino-acid is given. The product, which Posner obtained by the action of nitrous acid, was apparently impure tropic acid. We have repeated this action several times and find that it proceeds by no means smoothly. The gradual addition of potassium nitrite to the solution of the amino-acid in dilute hydrochloric acid caused the deposition of an oil, which was certainly not tropic acid, nor did it appear to be α-*iso*tropic acid, since it showed no signs of solidifying when nucleated with the latter acid. The aqueous solution was separated from the oil and extracted with ether. By crystallising the resulting acid several times from benzene, r-tropic acid was isolated in very small yield (0·1 g. of the pure acid, m. p. 116—117°, from 2 g. of β-aminohydratropic acid).

Resolution of r-β-*Chlorohydratropic Acid.*—The solution obtained by boiling 49·5 g. of morphine (1 mol.) in 820 c.c. of methyl alcohol was cooled to 42°, and 30 g. of r-β-chlorohydratropic acid (1 mol.; prepared from atropic acid: McKenzie and Wood, *loc. cit.*) were added in one instalment with vigorous stirring. The acid dissolved quickly. When the temperature had fallen to 39°, glassy prisms started to separate. After 18 hours in the ice-chest, 56 g. of solid were deposited. After the evaporation of the methyl alcohol from the filtrate, the acid obtained from the latter gave the following rotation in benzene : $l = 2$, $c = 3\cdot924$, $\alpha_D^{14°} + 3\cdot71°$, $[\alpha]_D^{14°} + 47\cdot3°$, so that the resolution had proceeded markedly after one crystallisation. The further progress is indicated as follows : 56 g. crystallised from 1350 c.c. of methyl alcohol $\longrightarrow$ 35 g., 850 c.c. of alcohol $\longrightarrow$ 19 g., 550 c.c. of alcohol $\longrightarrow$ 13 g., 400 c.c. of alcohol $\longrightarrow$ 9 g., 360 c.c. of alcohol $\longrightarrow$ 6 g. pure morphine l-salt. The solution of the crystals in methyl alcohol should be conducted as expeditiously as possible. The progress of the resolution was tested by the polarimetric examination of the acids obtained from the mother-liquors. The morphine salt, which separates in rectangular prisms, was decomposed by dilute sulphuric acid, the solution extracted with ether nine times, and the ethereal extract dried with anhydrous sodium sulphate. The resulting acid (2·1 g.), after drying in a vacuum until constant in weight, gave the following rotation in benzene :

$l = 2$, $c = 3.536$, $\alpha_D^{16°} - 8.66°$, $[\alpha]_D^{16°} - 122.4°$. The acid was crystallised from light petroleum (b. p. 60—80°), and gave a value for the rotatory power agreeing with the above within the limits of experimental error : $l = 2$, $c = 3.536$, $\alpha_D^{16°} - 8.67°$, $[\alpha]_D^{16°} - 122.6.°$

l-β-*Chlorohydratropic acid*, m. p. 62·5—63·5°, separates from light petroleum in rosettes of glassy plates. It is sparingly soluble in light petroleum, and readily so in ether, carbon disulphide, benzene, and ethyl alcohol (Found : Cl = 19·39. $C_9H_9O_2Cl$ requires Cl = 19·24%).

In acetone : $l = 2$, $c = 3.2300$, $\alpha_D^{15·5°} - 7.46°$, $[\alpha]_D^{15·5°} - 115.5°$.

Conversion of l-β-*Chlorohydratropic Acid into* l-*Tropic Acid.*— N-Sodium carbonate (11 c.c.) was gradually added (14 mins.) to a boiling solution of the l-acid (1 g.) in 20 c.c. of water (reflux). The boiling was continued for 3 hours, the cold solution extracted with ether to remove the styrene present, and the tropic acid obtained by acidification with dilute sulphuric acid and extraction with ether. Yield 0·7 g. In ethyl alcohol : $l = 2$, $c = 2.4348$, $\alpha_D^{15·5°} - 2.83°$, $[\alpha]_D^{15·5°} - 58.1°$.

A similar experiment was carried out with a lævorotatory acid having $[\alpha]_D^{16°} - 100.7°$ ($l = 2$, $c = 3.5504$) in benzene. The resulting tropic acid (1·9 g.) gave the following value in ethyl alcohol : $l = 2$, $c = 2.716$, $\alpha_D^{14°} - 2.68°$, $[\alpha]_D^{14°} - 49.3°$. After one crystallisation of this product from benzene, the value for the specific rotation was enhanced : in ethyl alcohol, $l = 2$, $c = 2.548$, $\alpha_D^{17°} - 3.17°$, $[\alpha]_D^{17°} - 62.2°$.

Conversion of l-β-*Chlorohydratropic Acid into* l-*Tropamide.*—A solution of the l-chloro-acid (0·94 g.) in 60 c.c. of aqueous ammonia (saturated at 0°) was kept for a week in a pressure flask at the ordinary temperature. When the solution was transferred to a crystallising dish, needles began to separate. Yield : 0·3 g.; m. p. 195—199° (Found : N = 8·7. Calc., N = 8·5%). In ethyl alcohol : $l = 2$, $c = 0.3472$, $\alpha_D^{17°} - 0.38°$.

In another experiment the resulting amide gave in ethyl alcohol : $l = 2$, $c = 0.3912$, $\alpha_D^{16°} - 0.43°$.

The concentrations employed were necessarily very small, the amide being sparingly soluble in water, ethyl alcohol, acetone, chloroform, benzene, and ethyl acetate.

For the purpose of comparison, the amide was prepared from l-tropic acid (obtained by resolution of the r-acid with morphine according to McKenzie and Wood) by acting on the ethyl ester with concentrated aqueous ammonia. After crystallisation from acetone, the amide had m. p. 195—197·5°; in ethyl alcohol : $l = 1$, $c = 0.377$, $\alpha_D - 0.24°$. Since the polarimetric determinations could be made with very dilute solutions only, we have no proof

that we obtained the optically pure *l*-tropamide by this method, more especially since there was always the possibility of partial racemisation having taken place during the action of ammonia on the *l*-ester. But we think it likely that we obtained the amide nearly pure, if not quite so.

l-Tropamide would be expected to undergo racemisation in the presence of a small amount of sodium ethoxide (McKenzie and Smith, J., 1922, **121**, 1348). When 0·5 c.c. of ethyl-alcoholic potash (0·6518N) was added to a solution giving $\alpha_D - 0.24°$ ($l = 1$), the lævorotation gradually dropped to zero after 30 hours, and *r*-tropamide (m. p. 170—171°) was isolated from the solution.

Formation of r-*Tropamide from* r-*Tropic Acid and* r-β-*Chlorohydratropic Acid.*—*r*-Tropic acid was converted into its methyl ester, from which the amide was prepared by the action of aqueous ammonia.

r-Tropamide, m. p. 170—171°, is sparingly soluble in cold water, ethyl alcohol, acetone, benzene, carbon tetrachloride, and light petroleum (b. p. 60—70°). It separates from water in needles (Found : $N = 8.4$. $C_9H_{11}O_2N$ requires $N = 8.5\%$).

A solution of *r*-β-chlorohydratropic acid (4 g.) in concentrated aqueous ammonia (65 c.c.) was kept for 18 days in a pressure flask. On pouring into a dish, crystallisation started quickly. The crystals (1·5 g.) were collected and crystallised twice from water, when the pure *r*-tropamide (m. p. 170—171°) was obtained (Found : $C = 65.1$; $H = 6.8$. Calc., $C = 65.4$; $H = 6.7\%$). The melting point was not depressed when this product was mixed with the *r*-tropamide obtained from methyl *dl*-tropate.

XV.—*Preparation of Quaternary Hydrocarbons.*

By EDWARD RUSSELL TROTMAN.

IN the course of some investigations in progress in this laboratory, certain quaternary hydrocarbons of the type $(C_6H_5\cdot CH_2)_2CR_1R_2$ were required, R_1 and R_2 being different alkyl radicals. No such compounds are known, and indeed very few quaternary hydrocarbons of any kind have been described. The interaction of Grignard reagents and tertiary halogen derivatives, which seemed

to offer a suitable method for their preparation, has already been studied. Gomberg and Cone (*Ber.*, 1906, **39**, 1461, 2975) succeeded in displacing the chlorine atom of triphenylmethyl chloride by various aromatic and aliphatic hydrocarbon radicals in this way. On the other hand, Davis and Kipping (J., 1911, **99**, 300) were unable to prepare γγ-dibenzyl-*n*-hexane, $(C_6H_5 \cdot CH_2)_2CEtPr$, by the action of magnesium propyl bromide on α-bromo-αα-dibenzyl-propane, $(C_6H_5 \cdot CH_2)_2CBrEt$; in every case, the product consisted mainly, if not entirely, of an unsaturated hydrocarbon. Späth (*Monatsh.*, 1913, **34**, 1965), who made an exhaustive study of the action of Grignard reagents on organic halogen derivatives, found that, although quaternary hydrocarbons were generally produced, the yield was always poor and a mixture of numerous products was obtained. It appeared, therefore, that the interaction of a Grignard reagent and a tertiary halide often takes quite an unexpected course and this conclusion is confirmed by the results described below.

A preliminary study of the proposed method was made with β-*bromo-α-phenyl-β-methylbutane*, a compound readily prepared from methyl ethyl ketone. This bromide reacted with magnesium ethyl bromide, with evolution of ethane and ethylene, but the product appeared to consist entirely of a mixture of the olefine, $C_6H_5 \cdot CH \colon CMeEt$, and the saturated compound, $C_6H_5 \cdot CH_2 \cdot CHMeEt$, and the possible presence of a small proportion of the quaternary hydrocarbon could not be proved. Attempts to prepare a quaternary hydrocarbon by first converting the bromide into a Grignard reagent and then treating the product with ethyl bromide were also unsuccessful; although the bromide reacted with magnesium in the presence of dry ether, magnesium bromide separated even at 0° and a mixture of the saturated hydrocarbon and the olefine was formed. β-*Bromo-α-phenyl-β-benzylpropane*, which was easily obtained in a pure crystalline form, reacted with magnesium ethyl bromide with formation of a small proportion of αδ-*diphenyl-βγ-dibenzyl-βγ-dimethylbutane* (compare Späth, loc. cit.) :

$$2CMeBr(CH_2Ph)_2 + 2MgEtBr = (CH_2Ph)_2CMe \cdot CMe(CH_2Ph)_2 + C_4H_{10} + MgBr_2.$$
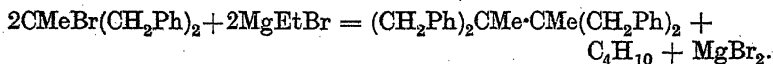
The main product, however, as indicated by analysis, and by the evolution of ethane and ethylene, was a mixture of αγ-*diphenyl-β-methylpropane* (I) (Graebe, *Ber.*, 1874, **7**, 1627), and an olefine, $C_{10}H_{16}$, believed to be αγ-diphenyl-β-methyl-Δα-propene (II) :

$$(I). \quad CHMe(CH_2Ph)_2 + C_2H_4 + MgBr_2 \xleftarrow{MgEtBr} CMeBr(CH_2Ph)_2 \xrightarrow{MgEtBr}$$
$$C_2H_6 + MgBr_2 + CHPh \colon CMe \cdot CH_2Ph \text{ (II.)}$$
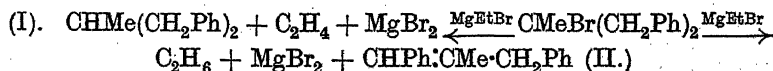
The constitution of this olefine could not be established by

oxidising it to a mixture of benzoic acid or benzaldehyde and benzyl methyl ketone with potassium permanganate or ozonised oxygen, since only benzoic acid was obtained; this result was doubtless due to the fact that benzyl methyl ketone is itself very readily oxidised. The structure assigned to the olefine is rendered very probable by the known behaviour of other bromides similar to β-bromo-α-phenyl-β-benzylpropane (compare Orechov and Konovalov, *Ber.*, 1912, **45**, 861; Orechov and Meerson, *ibid.*, p. 1926).

β-Bromo-α-phenyl-β-benzylpropane reacted with magnesium benzyl chloride with the formation of a very small quantity of the quaternary hydrocarbon, *α-phenyl-ββ-dibenzylpropane*. The main product, however, was an olefine, doubtless identical with II :

$$CMeBr(CH_2Ph)_2 + CH_2Ph \cdot MgCl = (II.) + MgClBr + C_6H_5 \cdot CH_3.$$
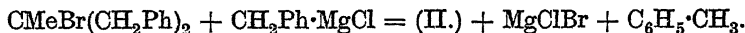
Unlike β-bromo-α-phenyl-β-methylbutane, β-bromo-α-phenyl-β-benzylpropane did not react with magnesium, even when iodine was added, so that the quaternary hydrocarbon could not be prepared by modifying the procedure. In boiling ethereal or benzene solution, the bromide reacted with sodium, but the above-described olefine was formed.

Tribenzylmethyl bromide (Schmerda, *Monatsh.*, 1909, **30**, 387), treated with magnesium ethyl bromide, gave a small yield of hexabenzylethane (Schmerda, *loc. cit.*), $2(CH_2Ph)_3CBr + 2MgEtBr = (CH_2Ph)_3C \cdot C(CH_2Ph)_3 + C_4H_{10} + 2MgBr_2$, but the main product was αγ-diphenyl-β-benzyl-$Δ^α$-propene (III) : $(CH_2Ph)_3CBr + MgEtBr = (III.) CHPh \colon C(CH_2Ph)_2 + C_2H_6 + MgBr_2$. This olefine, which has been described by Orechov and Grinberg (*J. Russ. Chem. Phys. Soc.*, 1916, **48**, 1713) as a viscous liquid, was obtained in well-formed crystals, m. p. 42—43°. Tribenzylmethyl bromide was also treated with magnesium benzyl chloride; it gave a small amount of *tetrabenzylmethane*, but the product consisted mainly of III. The action of zinc ethyl on this bromide was also investigated, but the above olefine was the only product.

As there seemed to be indications that the halogen atom of tertiary halides is more readily displaced by a benzyl than by an ethyl group, the action was investigated of magnesium benzyl chloride on *β-bromo-α-phenyl-β-methylpropane*. A quaternary hydrocarbon of the desired type, *viz.*, α-phenyl-β-benzyl-β-methyl-propane, was in fact produced, but about 50% of the product consisted of α-phenyl-β-methyl-$Δ^α$-propene (Klages, *Ber.*, 1904, **37**, 1721).

The results of these experiments show that in many cases the reaction between Grignard reagents and tertiary halogen derivatives does not follow the normal course. Späth (*loc. cit.*) expressed

the view that during this reaction the organic halide and the Grignard reagent undergo dissociation, so giving rise to free organic radicals :

$$R'X + RMgX = R' + R + MgX_2.$$
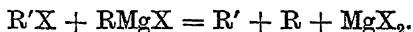
The existence of these radicals, however, is only momentary; those which are electropositive tend to unite together, but those which are more electronegative show a tendency to form olefines and paraffins containing the same number of carbon atoms as the radicals. The basis of Späth's classification into positive and negative radicals is not very obvious and his views do not seem to afford a very satisfactory explanation of the results summarised above.

A few attempts were made to obtain diketones of the type $C_6H_5 \cdot CO \cdot CR(CH_2 \cdot C_6H_5) \cdot CO \cdot CH_3$ in the hope that subsequent reduction might yield a quaternary hydrocarbon. *Benzylbenzoylacetone* was prepared, but on treatment with sodium ethoxide and ethyl bromide it gave ω-benzylacetophenone, an acetyl group being eliminated.

Experimental.

β-*Bromo-α-phenyl-β-methylbutane*, $C_6H_5 \cdot CH_2 \cdot CMeEtBr$, a colourless oil with a pleasant minty odour and an extremely irritating action on the eyes, was obtained in almost theoretical quantity by saturating benzylmethylethylcarbinol (Konovalov, *J. Russ. Chem. Phys. Soc.*, 1904, **36**, 228) with hydrogen bromide at the ordinary temperature. It decomposed when distilled even under 11 mm. and was therefore purified by washing it with dilute sodium carbonate solution and water (Found : Br = 34·0. $C_{10}H_{15}Br$ requires Br = 35·2%).

Action of Grignard Reagents on β-*Bromo-α-phenyl-β-methylbutane.* —When an excess of magnesium ethyl bromide was added to an ethereal solution of the bromide, a vigorous reaction immediately occurred, magnesium bromide was formed, and ethane and ethylene were evolved. The main product was an oil, practically the whole of which distilled between 195° and 205°. Its behaviour towards bromine and hydrogen bromide, and analyses of the bromo-derivatives thus obtained, indicated that it was a mixture of an olefine, believed to be α-phenyl-β-methyl-Δα-butene, and a saturated hydrocarbon, probably α-phenyl-β-methylbutane, b. p. 203—204° (Tafel and Hahl, *Ber.*, 1907, **40**, 3313). Since, from its boiling point, it could hardly contain an appreciable quantity of the expected quaternary hydrocarbon, and analysis showed the presence of a small proportion of benzylmethylethylcarbinol, the oil was not further examined.

A solution of the bromide in dry ether had no action on magnesium until a trace of iodine had been added; a vigorous reaction then set in and magnesium bromide separated even at 0°. The product was a mixture, b. p. 195—205°, apparently identical with that described above.

Dibenzylmethylcarbinol, $(C_6H_5 \cdot CH_2)_2CMe \cdot OH$, prepared from magnesium benzyl chloride and ethyl acetate, is a colourless, viscous, sweet-smelling liquid, b. p. 195—200°/14 mm. (with slight decomp.) (Found : C = 85·5; H = 8·0. $C_{16}H_{18}O$ requires C = 85·0; H = 8·0%).

β-*Bromo-α-phenyl-β-benzylpropane*, $(C_6H_5 \cdot CH_2)_2CMeBr$, obtained in good yield by saturating an ethereal solution of the unpurified carbinol with hydrogen bromide and recrystallising the product from light petroleum and from alcohol, formed well-defined, prismatic crystals, m. p. 78·5°. It loses hydrogen bromide when heated and cannot be distilled even under 0·2 mm. It is readily soluble in ether, alcohol, or benzene and sparingly so in light petroleum (Found : Br = 27·6. $C_{16}H_{17}Br$ requires Br = 27·7%).

Action of Magnesium Ethyl Bromide on β-*Bromo-α-phenyl-β-benzylpropane.*—A solution of the bromide in ether (1 vol.) was added slowly to magnesium ethyl bromide (4 vols.) at the ordinary temperature. The gas which was soon evolved, after being freed from ether with the aid of sulphuric acid, contained about 42% of ethane and 58% of ethylene. After 8 hours, the reaction mixture was boiled for 2 hours. The product, isolated in the usual way, was a slightly yellow oil. Its solution in alcohol (8 vols.) deposited crystals of αδ-*diphenyl-βγ-dibenzyl-βγ-dimethylbutane*,

$$(C_6H_5 \cdot CH_2)_2CMe \cdot CMe(CH_2 \cdot C_6H_5)_2,$$
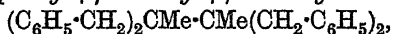
which separated from much light petroleum in colourless plates, m. p. 171°; the yield was about 0·5 g. from 40 g. of the bromide (Found : C = 92·0; H = 8·3; *M*, cryoscopic in benzene, = 389. $C_{32}H_{34}$ requires C = 91·9; H = 8·1%; *M* = 418).

Separation of αγ-*Diphenyl-β-methylpropane* (I) *and* (?) αγ-*Diphenyl-β-methyl-Δα-propene* (II).—The main product, obtained as an oil when the above alcoholic mother-liquor was evaporated, distilled between 290° and 300°. It combined with bromine in chloroform solution, but the dibromide did not crystallise and very readily lost hydrogen bromide. Oxidation or treatment with sulphuric acid having failed to separate the olefine from the saturated hydrocarbon, the oil was saturated with hydrogen bromide, when about 50% of it was converted into crystalline β-bromo-α-phenyl-β-benzylpropane. The unchanged oil was separated from the bromide and treated with sodium amalgam and aqueous alcohol to reduce any remaining bromide. The final

product, b. p. 290—294°, was α*γ-diphenyl-β-methylpropane* (Found :
C = 91·2; H = 8·4. $C_{16}H_{18}$ requires C = 91·4; H = 8·6%).
Thus the quaternary hydrocarbon, α-phenyl-β-benzyl-β-methyl-
butane (calc., C = 90·8; H = 9·2%), was not among the products
of the reaction.

The *olefine* (II), a colourless oil, b. p. 294—296°, was obtained
by boiling the bromide with an excess of pyridine for 8 hours.
It combined with bromine in chloroform solution, giving a di-
bromide which could not be crystallised and readily lost hydrogen
bromide when it was heated (Found : C = 92·2; H = 7·6. $C_{16}H_{16}$
requires C = 92·3; H = 7·7%).

Action of Magnesium Benzyl Chloride on β-*Bromo-α-phenyl-*
β-*benzylpropane.*—The Grignard reagent (4 mols.) did not react
with the bromide in ether at the ordinary temperature. The
ether was evaporated, and the residue heated at 100° for 2 hours.
The product, isolated in the usual way, was an oil, a solution of
which in alcohol deposited crystals of α-*phenyl-*ββ-*dibenzylpropane*,
$(C_6H_5\cdot CH_2)_3CMe$; these separated from alcohol in needle-shaped
prisms, m. p. 113°, which were sparingly soluble in alcohol or light
petroleum, but dissolved more readily in other organic solvents
(yield about 5%) (Found : C = 91·5; H = 7·9; *M*, cryoscopic
in benzene, = 294. $C_{32}H_{34}$ requires C = 92·0; H = 8·0%; *M* =
300). The main product, obtained as an oil when the alcoholic
mother-liquor was evaporated, contained the olefine (II), but the
probable presence of α*γ*-diphenyl-β-methylpropane (I) could not
be proved owing to the impossibility of separating the dibenzyl
which the oil contained.

Action of Magnesium Ethyl Bromide on Tribenzylmethyl Bromide.
—Tribenzylmethyl bromide (Schmerda, *loc. cit.*), which is most
conveniently prepared by saturating an ethereal solution of tri-
benzylcarbinol with hydrogen bromide, was treated in benzene
solution with an excess of ethereal magnesium ethyl bromide;
magnesium bromide separated at once and a gas, containing only
a very small proportion of olefine, was evolved. After 2 hours,
the reaction mixture was gently boiled for 1 hour. The product,
isolated in the usual way, was a very viscous oil; from its solution
in alcohol, colourless, cubical crystals gradually separated. This
compound, after recrystallisation from alcohol, melted at 42—
43° and was doubtless α*γ*-diphenyl-β-benzyl-Δ^{α}-propene (III) (com-
pare Orechov and Grinberg, *loc. cit.*). Its identity was established
by converting it into the crystalline dibromide, m. p. 127—128°,
and also into tribenzylmethyl bromide with the aid of hydrogen
bromide. When the alcoholic mother-liquor from the crystalline
olefine was evaporated, there remained an oil from which hexa-

benzylethane was isolated by converting the olefine into tribenzyl-methyl bromide (see above) and subsequently extracting the product with alcohol. From the alcoholic extract the hydrocarbon was deposited in crystals, m. p. 82—83°. Schmerda (*loc. cit.*) gives the m. p. 81—82° (Found : C = 92·4; H = 7·7. Calc. for $C_{44}H_{42}$, C = 92·6; H = 7·4%).

Tetrabenzylmethane, $C(CH_2 \cdot C_6H_5)_4$.—Tribenzylmethyl bromide, dissolved in benzene, was added to an ethereal solution of excess of magnesium benzyl chloride, the solvents were then evaporated, and the residue was heated at 100° for 2 hours. The product, isolated in the usual way, was an oil, from which *tetrabenzyl-methane* (yield 5%) was precipitated on the addition of alcohol. It separates from ether in cubic crystals, m. p. 164°, which are very sparingly soluble in alcohol or light petroleum, but dissolve more easily in other organic solvents (Found : C = 92·7; H = 7·5. $C_{29}H_{28}$ requires C = 92·5; H = 7·5%). The main product was αγ-diphenyl-β-benzyl-Δ^a-propene (III).

β-*Bromo-α-phenyl-β-methylpropane*, $C_6H_5 \cdot CH_2 \cdot CMe_2Br$, obtained by saturating dimethylbenzylcarbinol (Grignard, *Compt. rend.*, 1900, **130**, 1324) with hydrogen bromide and washing the product with sodium carbonate solution and water, is a colourless, pleasant-smelling liquid which loses hydrogen bromide very readily when it is warmed and does not distil unchanged under 11 mm. (Found : Br = 36·4. $C_{10}H_{13}Br$ requires Br = 37·5%).

α-*Phenyl-β-benzyl-β-methylpropane*, $(CH_2Ph)_2CMe_2$.—Reaction set in at once when the preceding bromide (1 mol.), dissolved in ether, was added to magnesium benzyl chloride (2 mols.); after 4 hours, the reaction mixture was boiled gently for 2 hours. The product, isolated in the usual way, consisted of an oil, which was separated by distillation into α-phenyl-β-methyl-Δ^a-propene, b. p. 181°, and a fraction of higher boiling point; the latter solidified when cold and crystallised from alcohol in prismatic needles, m. p. 68—69° (Found : C = 90·95; H = 9·0. $C_{17}H_{20}$ requires C = 91·1; H = 8·9%). α-*Phenyl-β-benzyl-β-methylpropane* boils at 293—294°, is readily soluble in most organic solvents, and has a somewhat sweet odour.

Benzylbenzoylacetone.—The sodium derivative of benzoylacetone, prepared from its constituents in ether, was isolated and boiled for 1 hour with an excess of benzyl chloride, the solution was filtered, and the unchanged benzyl chloride removed by distillation under reduced pressure. From an alcoholic solution of the residual dark brown oil, *benzylbenzoylacetone* was deposited in clusters of needle-shaped crystals, m. p. 60—61° (yield 50%). The compound is insoluble in aqueous potassium hydroxide and gives no coloration

with ferric chloride (Found: $C = 80 \cdot 6$; $H = 6 \cdot 1$. $C_{17}H_{16}O_2$ requires $C = 80 \cdot 95$; $H = 6 \cdot 35\%$). When an alcoholic solution of benzylbenzoylacetone containing sodium ethoxide and ethyl bromide is kept at the ordinary temperature for 24 hours, sodium bromide separates, but the product is mainly ω-benzylacetophenone.

The author desires to express his thanks to Professor F. S. Kipping, F.R.S., for suggesting this research, and for his interest in its progress.

XVI.—*Transformation of Mandelonitrile to Mandelo-isonitrile.*

By CHARLES EDMUND WOOD and HAROLD SAMUEL LILLEY.

MANDELONITRILE which has been kept for some time becomes viscous and in some cases deposits a dark yellow solid, owing to transformation of the normal nitrile to the *iso*-form; such material gives a poor yield (50%) of mandelic acid on hydrolysis.

The rate of change of the nitrile to the *iso*-form is variable and depends on the purity of the potassium cyanide used in its preparation. Crude commercial potassium cyanide gives products which remain clear for a long period (4—5 days), but 95% potassium cyanide (Poulenc Frères) yields a nitrile in which the rate of change is much greater. The following results show the maximum observed rate of change with time in the nitrile and the corresponding reduction in the yield of mandelic acid :—

Time (days)	0	0·25	0·5	0·75	1·0	2·0	3·0	4·0
% Yield of acid	94·6	91·0	86·5	82·0	78·1	65·0	56·4	50·3

The yields of acid obtained do not correspond with the composition of the mixture hydrolysed, owing to a reversion of the *iso* to the normal form under the conditions of hydrolysis. The results indicate that, to give the best yield of acid, the nitrile should be rapidly separated and hydrolysed (compare Pape, *Chem. Ztg.*, 1896, 20, 90).

The change of the nitrile on standing is continuous, no reaction product other than the yellow solid appears to be formed, and a nearly theoretical yield of the *iso*nitrile is ultimately obtained. The reversibility of the reaction is indicated by the hydrolysis of the pure *iso*nitrile, which yields 38% of mandelic acid.

A similar case is that of the *cyclo*hexane analogue of mandelonitrile. The colourless, oily hexahydrobenzaldehydecyanohydrin

(Zelinsky and Gutt, *Ber.*, 1908, **41**, 2677) becomes dark and viscous on standing, and when hydrolysed gives as main product a dark brown tar and little hexahydromandelic acid. Investigation of the tar showed that the *iso*nitrile was present in the product hydrolysed.

EXPERIMENTAL.

Formation of Mandeloisonitrile (α-Hydroxybenzylcarbylamine) from Mandelonitrile.—Mandelonitrile on keeping deposits mandeloiso-nitrile as a yellow solid which, after crystallisation from chloroform, melts at 196° (corr.) (Found : $N = 10\cdot7$; $M = 129$ in chloroform, 136 in carbon tetrachloride, 130 in camphor. Calc., $N = 10\cdot6\%$; $M = 133$). The *iso*nitrile is fairly soluble in alcohol, ether, or benzene, more soluble in carbon tetrachloride, and insoluble in water. It darkens on standing in air, is not attacked by alkali, but is rapidly decomposed by dilute or concentrated mineral acids. With concentrated sulphuric acid, it gives a bright green colour, whereas the normal nitrile gives a red one (Schiff, *Ber.*, 1899, **32**, 2701).

The *iso*nitrile structure was confirmed by reduction of the compound to a secondary base, oxidation to a carbimide, and by examination of its hydrolytic products.

This compound is distinct from the yellow solid, m. p. 206°, obtained by Minovici (*Ber.*, 1899, **32**, 2206) by the action of hydrogen chloride on an ethereal solution of mandelonitrile, for which the formula $C_6H_5\cdot CH(CN)\cdot C(OH)(CN)\cdot C_6H_5$ was suggested. Even after repeated crystallisation, our compound melted at the temperature stated; moreover, it differs from Minovici's compound in its solubility in alcohol and ether and in its inability to form a salt, m. p. 222°, with hydrochloric acid.

Reduction.—The *iso*nitrile (5 g.) was heated with a solution of 25 g. of " hydros " * in 100 c.c. of a mixture of equal parts of alcohol and water for 30 minutes on the water-bath, the excess of hydros decomposed with warm hydrochloric acid, and the liquid filtered into concentrated aqueous ammonia, when α-*hydroxybenzyl-methylamine*, $C_6H_5\cdot CH(OH)\cdot NH\cdot CH_3$, was precipitated.

The crude product was purified by conversion to the ether-insoluble picrate, decomposition of the salt with ammonia, and crystallisation of the liberated base from petroleum (b. p. 60—80°). The low yield (50%) is probably due to sulphamation during reduction. The base is a yellowish-grey solid, m. p. 180° (decomp.), readily soluble in alcohol, ether, or mineral acids (Found : $N = 10\cdot3$. $C_8H_{11}ON$ requires $N = 10\cdot2\%$). The *nitrosoamine*, prepared in the

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* Stannous chloride or ammonium chloride and zinc dust may be employed.

usual way, is a yellow oil which solidifies on cooling. The *picrate*, prepared in ethereal solution, is a dark yellow, crystalline solid, m. p. 238° (decomp.) (Found : Picric acid = 62·1. $C_8H_{11}ON,C_6H_3O_7N_3$ requires 62·7%).

Oxidation.—An ethereal or carbon tetrachloride solution of the *iso*nitrile was heated with mercuric oxide (theor. quantity) on the water-bath for 1 hour. The dark red oil of disagreeable odour obtained on evaporating the filtered solution changed, on standing, to a black, amorphous mass, probably a polymeride. The oily carbimide could not be purified for analysis, but its structure was established by means of its reaction products.

The oil was treated with gaseous ammonia in carbon tetrachloride solution, when the red colour rapidly disappeared. The solution, on evaporation, deposited almost colourless crystals of the *carbamide*, $C_6H_5 \cdot CH(OH) \cdot NH \cdot CO \cdot NH_2$, m. p. 76° (Found : N = 16·95. Theory requires N = 16·9%), readily soluble in water or alcohol, less soluble in benzene. The *nitrate* is fairly soluble in water, but mercuric chloride precipitates from neutral aqueous solutions the slightly yellow, almost insoluble *mercurichloride*,

$$C_6H_5 \cdot CH(OH) \cdot NH \cdot CO \cdot NH_2, HgCl_2$$
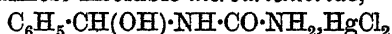
(Found : Hg = 45·58. Theory requires Hg = 45·83%).

The *picrate*, prepared in ethereal solution, was obtained as an orange, crystalline solid, easily soluble in ether or alcohol [Found : picric acid = 73·6. $C_6H_5 \cdot CH(OH) \cdot NH \cdot CO \cdot NH_2, 2C_6H_3O_7N_3$ requires 73·3%].

Hydrolysis.—The *iso*nitrile rapidly dissolved when treated on the water-bath with concentrated hydrochloric acid (5 parts). The small quantity of tarry matter produced was removed, the filtrate distilled in steam, and benzaldehyde extracted from the distillate, which then showed, after neutralisation, the characteristic reducing properties of formic acid.

The benzaldehyde is produced by the decomposition of the primary base initially formed in the hydrolysis, which may be represented as follows :

$$OH \cdot CHPh \cdot NC \longrightarrow H \cdot CO_2H + OH \cdot CHPh \cdot NH_2 \longrightarrow Ph \cdot CHO + NH_3.$$
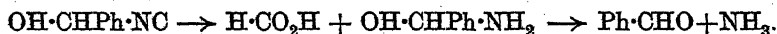
The amounts of formic acid and benzaldehyde found were not theoretical; in addition to the tarry matter deposited, a certain amount of mandelic acid was extracted.

By the hydrolysis of the pure *iso*nitrile for 3 hours under the above conditions, a 38% yield of mandelic acid was obtained. The mandelic acid was estimated by neutralisation of the filtered reaction product with ammonia, followed by addition of zinc sulphate or cadmium chloride solution; zinc or cadmium mandelate,

precipitated on standing and shaking, was filtered off, dried, and weighed. Small corrections (McKenzie, J., 1899, **75**, 969) were applied for the solubility of these salts. The use of the silver salt in the estimation is precluded owing to the presence of formic acid, and to a lesser extent, benzoic acid. Hence the reaction normal nitrile → *iso*nitrile is reversible, proceeding under the conditions of hydrolysis from the *iso* to the normal form (compare Guillemard, *Compt. rend.*, 1907, **144**, 141). Further, when mixtures of the two forms are hydrolysed, the yield of mandelic acid is greater than that corresponding with the initial composition of the mixture. Also, on allowing the normal nitrile to stand, the yield of acid on hydrolysis cannot fall below 38%, although the change to the *iso*-form is complete.

The observed tarry matter consists probably of compounds produced by the action of ammonia on the nitrile (Schiff, *Ber.*, 1899, **32**, 2701).

Hydrolysis of Hexahydromandeloisonitrile.—The pure *iso*nitrile has not been isolated, but the normal form, kept for 2 months and then hydrolysed, gave large amounts of tarry matter and 20% of acid. The tarry product was polymerised hexahydrobenzaldehyde and its ammonia derivative, for by treatment with dilute caustic soda solution, followed by distillation in steam after acidification, the aldehyde was extracted from the distillate in quantity. Formic acid accompanied the viscous products.

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XVII.—*The Hydrolysis of Acylchloroamines in Water.*

By FREDERICK GEORGE SOPER.

THE slight extent of the reversible hydrolysis of chloroamines in water (Orton and Gray, *Brit. Assoc. Rep.*, 1913, 135), $:NCl + H_2O \rightleftharpoons :NH + HClO$, renders its quantitative study difficult, since it necessitates direct estimation of the concentrations of the hydrolysis products (as opposed to their estimation by difference), and, further, neither of the hydrolysis products is a sufficiently good electrolyte to allow of the application of sensitive electrical methods. Moreover, the one partition method available, that of estimation of the hypochlorous acid by distillation (Orton and Gray, *loc. cit.*), is, as will be shown later, complicated by the fact that the chloroamine is itself volatile.

In order to increase the hydrolysis of a chloroamine and thus

allow of the general application of methods available for the examination of homogeneous equilibrium, the concentration of one of the products of the hydrolysis may be still further reduced by its reversible combination with some other substance, the conditions of equilibrium with which are known. Substances considered for this purpose were hydrochloric acid, interacting with the hypochlorous acid to form chlorine, or an alkali, forming hypochlorite. Both these substances, however, may cause secondary reactions, the chlorine forming C-chlorinated products, whilst the alkali may cause hydrolysis of, and to a certain extent may form complexes with, the acylamine present. The use of another amine, which forms reversibly a chloroamine with the hypochlorous acid present, is free from the objections associated with the use of hydrochloric acid or an alkali, but it demands a knowledge of the hydrolysis equilibrium of *one* chloroamine before calculation of other hydrolysis constants becomes possible. p-Toluenesulphondichloroamide was selected as this standard chloroamine for reasons that have already been given (J., 1924, **125**, 1899).

When the hydrolysis of the chloroamine under investigation has been displaced, the method of examination employed is of a solubility type, and depends on the following considerations. p-Toluenesulphondichloroamide dissolves in solutions of anilides with the formation of the corresponding chloroamines :

$$C_7H_7 \cdot SO_2 \cdot NCl_2 + H_2O \underset{\displaystyle C_7H_7 \cdot SO_2 \cdot NH_2}{\overset{\displaystyle C_7H_7 \cdot SO_2 \cdot NHCl}{\Big\langle}} + HClO \xrightarrow{\text{ArAcNH}} \text{ArAcNCl.}$$
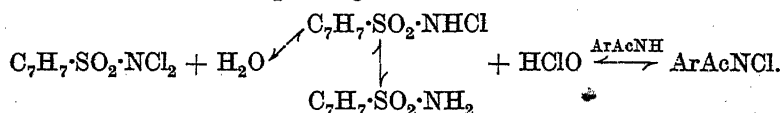
Hypochlorous acid is removed by combination with the added anilide and causes further solution and hydrolysis of the sulphondichloroamide. From the increase in the solubility of the sulphondichloroamide, as measured by the thiosulphate titre of the saturated solution, the concentrations of the chloroamines formed in solution can be calculated. This " solubility " of the sulphondichloroamide n a solution of an anilide is made up of the concentrations of the dichloroamide, the monochloroamide, the chloroamine formed from the anilide, and the hypochlorous acid. If a is the equilibrium concentration of the dichloroamide in millimols. in solution, T_1 the thiosulphate titre expressed as milliequivalents per litre, then

$$[C_7H_7 \cdot SO_2 \cdot NHCl] + [ArAcNCl] + [HClO] = (T_1 - 4a)/2,$$

or neglecting the [HClO], for reasons discussed below, and denoting the concentration of the chloroamine, ArAcNCl, formed from d millimols. of anilide by x and that of the sulphonmonochloroamide by b,

$$x + b = (T_1 - 4a)/2 = S \quad . \quad . \quad . \quad . \quad (1)$$

It is known that (J., 1924, **125**, 1906) at 25°,

$$[C_7H_7 \cdot SO_2 \cdot NHCl][HClO] = 8 \cdot 0 \times 10^{-4} \, [C_7H_7 \cdot SO_2 \cdot NCl_2]$$
$$= 6 \cdot 27 \times 10^{-5} \quad . \quad . \quad . \quad . \quad (2)$$

and $[C_7H_7 \cdot SO_2 \cdot NH_2][HClO] = 4 \cdot 9 \times 10^{-5} \, [C_7H_7 \cdot SO_2 \cdot NHCl]$ (3)

while from the general conditions of equilibrium

$$[C_7H_7 \cdot SO_2 \cdot NH_2] = x - b \quad . \quad . \quad . \quad . \quad (4)$$

Combining (3) and (4),

$$[HClO](x - b)/b = 4 \cdot 9 \times 10^{-5};$$

eliminating HClO from (2),

$$(x - b)/b^2 = 0 \cdot 781 ;$$

and eliminating x from (1),

$$0 \cdot 781 b^2 + 2b - S = 0 \quad . \quad . \quad . \quad . \quad (5)$$

This equation allows of the calculation in millimols., of b, of the concentration of hypochlorous acid, from (2), and of that of the chloroamine formed, from (1). The hydrolysis constant is given by the expression $[HClO][\text{anilide}]/[\text{chloroamine}] = [HClO]x/(d - x)$.

The omission of the hypochlorous acid concentration from equation (1) is permissible, because the progressive hydrolysis of the dichloroamide, caused by combination between the anilide and hypochlorous acid, results in an increase in the concentration of its hydrolysis product, $C_7H_7 \cdot SO_2 \cdot NHCl$, and hence in a diminution of the concentration of the hypochlorous acid, initially only 0·0079 millimols., since in presence of one solid phase, *viz.*, the sulphondichloroamide, the expression $[HClO][C_7H_7 \cdot SO_2 \cdot NHCl]$ is constant. It is this reduction in the concentration of the hypochlorous acid that makes the method of extensive use. For since the equilibrium concentration of the amine is measured by a difference, $d - x$, it is necessary that $x(= [ArAcNCl])$ should not approach d (the concentration of the anilide initially present) too closely in value, *i.e.*, the hydrolysis of the chloroamine should always be extensive. This is effected by the automatic diminution of the concentration of the hypochlorous acid, for the smaller the hydrolysis constant of the chloroamine (and therefore the greater the need for the displacement of its hydrolysis equilibrium), the smaller does the concentration of hypochlorous acid become, due to the accumulation of the sulphon*mono*chloroamide in the system.

The hydrolysis constants of the chloroamines of acetanilide, formanilide, aceto-*o*- and -*p*-toluidides, and *o*- and *p*-chloroacetanilides have been determined. The details of one determination and the mean values of K_h in the other cases are given in Table I.

TABLE I.

N-Chloroacetanilide.

Conc. of anilide $\times 10^3$.	Thio. titre of sat. soln. $\times 10^3$.	b in $M \times 10^{-3}$.	x in $M \times 10^{-3}$.	HClO $M \times 10^{-7}$.	$K_h \times 10^7$.
0·5M	0·996N	0·161	0·182	3·89	6·80
1·0	1·322	0·232	0·274	2·70	7·15
2·0	1·784	0·317	0·420	1·88	7·44
5·0	2·734	0·506	0·706	1·24	7·53
				Mean	7·27

	$K_h \times 10^7$.		$K_h \times 10^7$.
N-Chloroformanilide	2·4	No-Dichloroacetanilide	6·9
N-Chloroaceto-o-toluidide ...	3·3	Np-Dichloroacetanilide	15·0
N-Chloroaceto-p-toluidide ...	22·0		

In Table II, the hydrolysis constants of the chloroamines examined are compared with the ionisation constants of similarly substituted compounds and with the equilibrium constants of the hydrolysis of anilides into amine and acid (MacBain and Davies, *Z. physikal. Chem.*, 1911, **78**, 369).

TABLE II.

Group.	K_h (chloro-amine).	K (anilide).	K_b (amine).	$1/K_a$ (phenol).	$1/K_a$ (benzoic acid).
H	$0·73 \times 10^{-6}$	4·1	$4·6 \times 10^{-10}$	$7·5 \times 10^5$	$16·7 \times 10^3$
o-CH$_3$	0·33	1·7	3·3	—	8·3
p-CH$_3$	2·2	6·4	20·0	—	19·4
o-Cl	0·69	0·14	—	1·3	0·76
p-Cl	1·5	2·2	1·3	2·5	10·7

The relative effects of the o-methyl and the p-methyl groups on the hydrolysis of the chloroamines and the ionisation of the amines are almost identical, as are also the relative effects of the o-chlorine and the p-chlorine atoms on the chloroamines and the phenols. The influence of the chlorine atom, compared with that of the hydrogen atom, on the hydrolysis of the chloroamines does not, however, appear to be similar to its influence on the ionisation of other substances.

The volatility of the chloroamine when its aqueous solutions are subjected to distillation at 25° causes the estimate of the percentage of free hypochlorous acid in an aqueous solution of N-chloroacet-anilide (Orton and Gray, *loc. cit.*) to be high. Thus, on addition of successive quantities of acetanilide to the aqueous chloroamine solution, the ratio of the thiosulphate titre of the distillate to that of the original solution decreases to a minimum value of 0·20, independent of the concentration of the chloroamine solution. This behaviour is unlike that observed in the distillation of sodium hypochlorite in presence of excess of sodium hydroxide, the titre of the distillate then falling to zero. The thiosulphate titre of the distillate obtained from a 0·1% solution of N-chloroacetanilide was found (Orton and Gray, *loc. cit.*) to be 0·00268N, which, after

allowing for the volatility of the chloroamine, corresponds to a concentration of 0·00016 mol. of hypochlorous acid in the distillate or 5·94 × 10⁻⁵ mol. of hypochlorous acid in the chloroamine solution. The calculated hydrolysis constant of N-chloroacetanilide is then 6·0 × 10⁻⁷, a satisfactory confirmation of the value obtained by the solubility method (7·3 × 10⁻⁷).

The limited solubility of anilides in water has prevented extensive examination in this medium. The primary object has been the determination of a few hydrolysis constants as a basis for testing theories of the mechanism of the chloroamine–chloroanilide transformation. The effect of substituents on the hydrolysis is being examined in other media.

<div align="center">EXPERIMENTAL.</div>

Determination of the Solubility.—The determination of the solubility of p-toluenesulphondichloroamide in solutions of anilides was carried out in the same way as that in aqueous solutions of p-toluenesulphonamide (Soper, *loc. cit.*). The solution attained a practically constant titre after 3—6 hours. Since the chloroamines of anilides decompose slowly in water, owing to hydrolysis of the anilides to anilines (Orton and Gray, *loc. cit.*), one molecule of which removes a number of molecules of hypochlorous acid, the concentration of hypochlorous acid falls, and since the expression

$$[HClO][C_7H_7 \cdot SO_2 \cdot NHCl]$$
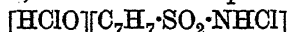
is constant in presence of the solid dichloroamide, the concentration of the monochloroamide increases. The net result is that the titre of the solution slowly increases on standing (*i.e.*, after 24 hours). The following figures, obtained during the solution of the dichloroamide in a solution of acetanilide (2M × 10⁻³), are typical.

Time	2	4	6	12	24 hours
Titre of 20 c.c. in N/500-thio.	13·71	17·80	17·86	17·92	18·05 c.c.

Distillation of Aqueous Chloroamine Solutions.—The diagram of the apparatus used has been given elsewhere (Soper, J., 1924, **125**, 2230). The thiosulphate titre of the solutions was taken before and after the distillation. There was no appreciable change during this process. No further decrease in the ratio of the titre of the distillate to that of the solution was obtained on increasing the acetanilide concentration from 0·02M to 0·05M.

XVIII.—*The Action of Amines on Semicarbazones. Part II.*

By FORSYTH JAMES WILSON and ARCHIBALD BARCLAY CRAWFORD.

IN continuation of previous work (J., 1922, **121**, 866) we have found that *l*-menthylamine reacts normally with acetonesemicarbazone to give active *acetone-δ-menthylsemicarbazone*, $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + C_{10}H_{19}{\cdot}NH_2 = NH_3 + CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{19}$, from which *δ-menthylsemicarbazide*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_{19}$, and its *hydrochloride* have been obtained. These compounds, including the benzaldehyde derivative, are lævorotatory in alcoholic solution.

The action of esters of amino-acids on semicarbazones was next investigated. Ethyl *m*-aminobenzoate and acetonesemicarbazone reacted normally on heating, $CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}C_6H_4{\cdot}CO_2Et = CMe_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et + NH_3$, giving *acetone-δ-3-carbethoxyphenylsemicarbazone* in good yield, from which *δ-3-carbethoxyphenylsemicarbazide*, $NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et$, and its *hydrochloride* were obtained. Ethyl *p*-aminobenzoate also reacted normally with benzophenone- and acetone-semicarbazone (in the latter case with poor yield), giving the ketonic *δ-4-carbethoxyphenylsemicarbazones*, $CR_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et$, both of which underwent complete decomposition when hydrolysis was attempted.

Methyl *o*-aminobenzoate reacted somewhat differently. In view of what follows, care was taken in all these cases to use dry materials and dry solvents so as to avoid any risk of hydrolysis. The ester, on heating with benzophenonesemicarbazone (molecular quantities), gave 3-*diphenylmethyleneaminotetrahydroquinazoline*-2 : 4-*dione* (I),

$$C_6H_4{<}{\substack{NH_2 \\ CO_2Me}} + NH_2{\cdot}CO{\cdot}NH{\cdot}N{:}CPh_2 = NH_3 + MeOH +$$

$$C_6H_4{<}{\substack{NH{\cdot}CO \\ CO-N{\cdot}N{:}CPh_2,}} \quad \text{(I.)}$$
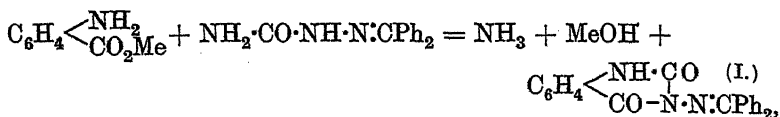
this, on hydrolysis with acid, giving benzophenone and 3-amino-tetrahydroquinazoline-2 : 4-dione (II), $C_6H_4{<}{\substack{NH{\cdot}CO \\ CO-N{\cdot}NH_2,}}$ described by Kunckell (*Ber.*, 1910, **43**, 1021). In addition, methyl alcohol, benzophenonecarbohydrazone (III), tetrahydroquinazoline-2 : 4-dione (IV), and small quantities of diphenyl ketazine and hydrazodicarbonamide were produced.

Borsche and Merkwitz have shown (*Ber.*, 1904, **37**, 3177) that benzophenonesemicarbazone, on heating, gives (III), presumably by interaction with the hydrazone, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 + NH_2{\cdot}N{:}CPh_2 = NH_3 + CO(NH{\cdot}N{:}CPh_2)_2$ (III), the hydrazone appar-

ently resulting from the semicarbazone by loss of cyanic acid, $CPh_2:N\cdot NH\cdot CO\cdot NH_2 = CPh_2\cdot N\cdot NH_2 + HNCO$. In the present instance, the formation of (III) and (IV), the latter investigated, among others, by Griess (*Ber.*, 1869, 2, 416), can be explained as resulting from the ester and the semicarbazone,

$$C_6H_4{<}^{NH_2}_{CO_2Me} + {}^{NH_2\cdot CO\cdot NH\cdot N:CPh_2}_{NH_2\cdot CO\cdot NH\cdot N:CPh_2} = NH_3 + MeOH +$$

$$C_6H_4{<}^{NH\cdot CO\cdot NH\cdot N:CPh_2}_{CO\cdot NH\cdot CO\cdot NH\cdot N:CPh_2},$$
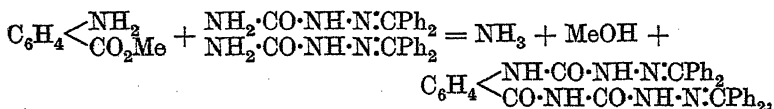
which then gives (III) and (IV), the diphenyl ketazine and the hydrazodicarbonamide being produced by the decomposition of the semicarbazone as shown by Borsche and Merkwitz,
$2CPh_2:N\cdot NH\cdot CO\cdot NH_2 = CPh_2:N\cdot N:CPh_2 + NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$.
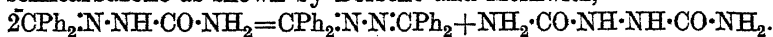
The interaction of acetonesemicarbazone with methyl *o*-aminobenzoate proceeded quite abnormally : as before, molecular quantities were employed and care was taken to use dry solvents. The acetone derivative (V) expected from the scheme $CMe_2:N\cdot NH\cdot CO\cdot NH_2$

$$+ C_6H_4{<}^{NH_2}_{CO_2Me} = NH_3 + MeOH + C_6H_4{<}^{NH\cdot CO}_{CO-N\cdot N:CMe_2}\quad (V),$$
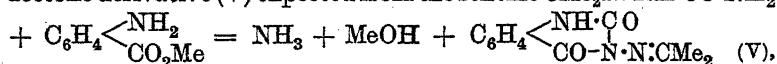
was not produced; the products were ammonia, methyl alcohol, 3-aminotetrahydroquinazoline-2 : 4-dione (II) (the chief solid product, amounting to about half of the semicarbazone used), a considerable amount of dimethyl ketazine, small quantities of tetrahydroquinazoline-2 : 4-dione (IV) and of a *substance*, m. p. 420°, which could not be identified; it is noteworthy that no hydrazodicarbonamide was formed.

A different explanation is necessary in this case. It may be assumed that (V) 3-iso*propylideneaminotetrahydroquinazoline*-2 : 4-*dione* (prepared by another method and described below) is first produced with formation of ammonia and methyl alcohol and that it may react further in one of two ways. It may decompose as follows,

$$2C_6H_4{<}^{NH\cdot CO}_{CO-N\cdot N:CMe_2} = CMe_2:N\cdot N:CMe_2 +$$

$$C_6H_4{<}^{NH\cdot CO\ CO\cdot NH}_{CO-N-N--CO}{>}C_6H_4\quad (VI.)$$
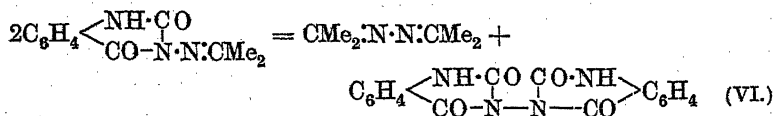
A substance of the composition represented by (VI) was not obtained (the unidentified substance of m. p. 420° giving quite different analytical results); moreover it was found, as mentioned later, that (V) did not behave in this way on heating. The other possibility, and the one which we regard as the probable explanation, is that (V) reacts with acetonesemicarbazone to give dimethyl ketazine and the intermediate carbamino-derivative (VII),

$$C_6H_4 \overset{NH \cdot CO}{\underset{CO-N \cdot N:CMe_2}{\big<}} + NH_2 \cdot CO \cdot NH \cdot N:CMe_2 = CMe_2:N \cdot N:CMe_2 +$$

$$C_6H_4 \overset{NH \cdot CO}{\underset{CO-N \cdot NH \cdot CO \cdot NH_2}{\big<}} \quad \text{(VII.)}$$
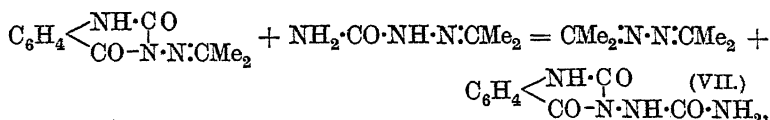
which then by loss of cyanic acid gives (II).

Borsche and Merkwitz (*loc. cit.*) apparently assume loss of cyanic acid in a similar case. Auwers and others (*Annalen*, 1924, **435**, 277) have shown that tetrahydroindazole-2-carbonamide loses cyanic acid (identified as cyanuric acid) on heating at 160°,

$$C_6H_4 \overset{CH}{\underset{N}{\lll}}N \cdot CO \cdot NH_2 \rightarrow C_6H_4 \overset{CH}{\underset{N}{\lll}}NH.$$ Similarly, Posner (*Ber.*,

1901, **34**, 3976) found that compounds of the type $\underset{NH_2 \cdot CO \cdot N\underline{\quad\quad}N}{RC:CH \cdot CR}$
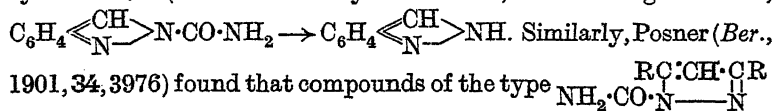
(R = alkyl), obtained from semicarbazide and diketones, give

with silver nitrate the derivative $\underset{AgN\underline{\quad\quad}N}{RC:CH \cdot CR}$: when R = Ph,

the carbamino-compound is not formed on heating the reactants, the product being 3 : 5-diphenylpyrazole. The substance (IV) probably results, together with (II), by interaction of (VII) with the ester :

$$C_6H_4 \overset{NH \cdot CO}{\underset{CO-N}{\big<}} \overset{NH_2}{\underset{NH}{\overset{|}{CO}}} + \overset{MeCO_2}{\underset{NH_2}{>}} C_6H_4 =$$

$$\text{(IV.)}\ C_6H_4 \overset{NH \cdot CO}{\underset{CO-NH}{\big<}} + \text{(II.)}\ C_6H_4 \overset{NH \cdot CO}{\underset{CO-N \cdot NH_2}{\big<}} + MeOH.$$
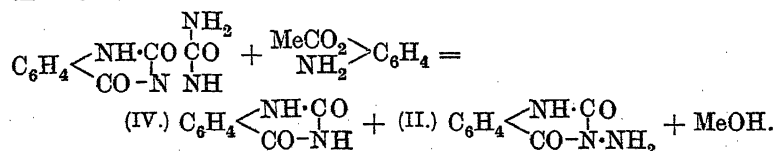
To test these explanations, (V) was prepared by boiling ordinary undried acetone with (II); curiously enough, dried acetone did not react even on prolonged boiling, ββ-dichloropropane also proved unreactive. This substance (V) was easily hydrolysed into the parent compounds by water and by hot solvents containing water. It was scarcely affected by heating even at 220° for 2½ hours, it charred slightly and there was a slight odour of dimethyl ketazine, but most of the substance was recovered unchanged. Molecular quantities of (V) and acetonesemicarbazone, on heating, gave dimethyl ketazine and (II), this being in accordance with the explanation advanced by us.

This work will be continued.

EXPERIMENTAL.

1-*Menthylamine and Acetonesemicarbazone.*—The *l*-menthylamine, prepared by the method of Beckmann (*Annalen*, 1889, **250**, 325) and of Wallach (*ibid.*, 1893, **276**, 327), was distilled directly in a current of hydrogen into a polarimeter tube; it gave $[\alpha]_D^{20} - 39 \cdot 41°$

E*

[Wallach records — 38·07°; Tutin and Kipping (J., 1904, 85, 69) record — 39·92°].

Equimolecular quantities, previously heated to 165°, were mixed and kept at this temperature for 15 minutes, when solution with copious evolution of ammonia took place. The cooled melt, dissolved in a little alcohol, was poured into dilute acetic acid, the solid which separated dissolved completely in hot alcohol, from which, on cooling, active *acetone-δ-menthylsemicarbazone* was deposited in clusters of small, colourless needles, m. p. 128° (Found : $N = 16·62$, $16·73$. $C_{14}H_{27}ON_3$ requires $N = 16·60 \%$). $0·5024$ Gram in 25 c.c. of absolute alcohol gave $\alpha_D^{20°} - 2·612°$ ($l = 2$), whence $[\alpha]_D^{20°} - 64·93°$. Yield 65 %. The substance was soluble in the usual organic solvents.

Active δ-*Menthylsemicarbazide.*—The semicarbazone was heated at 70° with N-hydrochloric acid (5 parts) until completely dissolved ; the residue obtained by evaporation under reduced pressure was recrystallised from alcohol, which gave δ-*menthylsemicarbazide hydrochloride* as a gelatinous mass ; after suction and washing with ether, it assumed a fibrous, apparently non-crystalline appearance and melted at 203—204° (Found : $Cl = 14·02, 14·22$. $C_{11}H_{23}ON_3,HCl$ requires $Cl = 14·22\%$). $0·5024$ Gram in 25 c.c. of absolute alcohol gave $\alpha_D^{20°} - 2·62°$ ($l = 2$), whence $[\alpha]_D^{20°} - 65·18°$. It was soluble in alcohol or hot water, insoluble in ether or benzene, and could not be obtained in a definitely crystalline form. δ-*Menthylsemicarbazide*, obtained by dissolving the hydrochloride in hot dilute alcohol, adding sodium hydroxide solution in slight excess, and then immediately diluting and cooling in ice, crystallised from light petroleum containing a little benzene in microscopic prisms, m. p. 138° (Found : $N = 19·89, 19·83$. $C_{11}H_{23}ON_3$ requires $N = 19·71\%$). $0·4994$ Gram in 25 c.c. of absolute alcohol gave $\alpha_D^{20°} -3·11°$ ($l = 2$), whence $[\alpha]_D^{20°} - 77·94°$. It was soluble in the usual organic solvents on heating : solutions cannot be kept, as they become green after one day. Addition of ethereal hydrogen chloride in slight excess to an absolute alcoholic solution precipitated the gelatinous hydrochloride. The *benzylidene* derivative, obtained by shaking an alcoholic solution of the hydrochloride with a little benzaldehyde and then adding a little water, solidified on standing and crystallised from alcohol, in which it was very soluble, in fine, rhombic prisms, m. p. 111° (Found : $N = 13·96$. $C_{18}H_{27}ON_3$ requires $N = 13·95\%$). $1·898$ Grams in 100 c.c. of absolute alcohol gave $\alpha_D^{20°} - 1·79°$ ($l = 2$), whence $[\alpha]_D^{20°} - 47·18°$. Solutions became green on standing.

Ethyl m-*Aminobenzoate and Acetonesemicarbazone.*—The two substances (1·6 mols. of the latter) were heated at 165° until the

evolution of ammonia began to slacken (20 minutes). The cooled melt was gently heated with a little alcohol, which, after filtration from hydrazodicarbonamide, deposited a solid on cooling; this was washed with a little alcohol and recrystallised from this solvent. A little more hydrazodicarbonamide was deposited followed by colourless plates of *acetone-δ-3-carbethoxyphenylsemicarbazone*, m. p. 146° (Found: N = 15·94, 16·02. $C_{13}H_{17}O_3N_3$ requires N = 15·97%). It was moderately soluble in alcohol, very soluble in pyridine, sparingly soluble or insoluble in other solvents. Yield 80%. Hydrolysis was effected by covering the substance with $2\frac{1}{2}N$-hydrochloric acid and warming to 70°; the solid which separated on cooling in ice gave, after recrystallisation from alcohol, prisms of *δ-3-carbethoxyphenylsemicarbazide hydrochloride*, m. p. 172° (Found: Cl = 13·56, 13·72. $C_{10}H_{13}O_3N_3$,HCl requires Cl = 13·68%); it was readily soluble in hot (not very soluble in cold) water and hot alcohol, and reduced Fehling's solution and ammoniacal silver nitrate. *δ-3-Carbethoxyphenylsemicarbazide*, prepared in the usual manner from this salt with sodium hydroxide, separated from benzene in small prisms, m. p. 119°; it was very soluble in alcohol, chloroform, or hot benzene, and sparingly soluble in water (Found: N = 18·87, 18·88. $C_{10}H_{13}O_3N_3$ requires N = 18·83%). The *benzylidene* derivative, prepared from a hot aqueous solution of the hydrochloride and benzaldehyde, separated from alcohol in fine, hair-like needles, m. p. 144°, very soluble in most solvents except water (Found: N = 13·62, 13·50. $C_{17}H_{17}O_3N_3$ requires N = 13·50%).

Ethyl p-*Aminobenzoate and Benzophenonesemicarbazone.*—The semicarbazone was added during 1 hour to the ester (2 mols.) heated at 230°; a gentle evolution of ammonia took place and the heating was continued for 15 minutes after the last addition. The alcoholic extract of the cooled melt, after filtering from hydrazodicarbonamide, was poured into dilute acetic acid to remove excess of ester. The solid which separated on standing was extracted with cold toluene; the insoluble portion on recrystallisation from benzene gave pearly plates of *benzophenone-δ-4-carbethoxyphenyl-semicarbazone*, m. p. 168° (Found: N = 11·03, 10·68. $C_{23}H_{21}O_3N_3$ requires N = 10·85%). The toluene extract contained diphenyl ketazine and benzophenonecarbohydrazone. The substance was soluble in most organic solvents, but almost insoluble in cold benzene, toluene, or light petroleum; exposure to light converted it without change of melting point into a lemon-yellow modification which gave colourless solutions. Yield about 57%.

Ethyl p-*Aminobenzoate and Acetonesemicarbazone.*—The semicarbazone was added during 20 minutes to the ester (1 mol. of

E* 2

each) heated at 190—200°. The alcoholic extract of the cooled melt, filtered from a small amount of hydrazodicarbonamide, was evaporated, and the residue recrystallised from alcohol. The crystals obtained were washed with cold acetone to dissolve a small quantity of a *substance* which was not identified (prisms from acetone, m. p. 130°; found, N = 14·2%); several recrystallisations from alcohol gave hexagonal tablets of *acetone-δ-4-carbethoxyphenyl-semicarbazone*, m. p. 194°. There was some difficulty in separating it from a very small amount of a powdery *substance*, m. p. 210°, which had almost the same solubility. The estimation of nitrogen in the semicarbazone offered considerable difficulty, the results being high and not concordant, due possibly to the production of methane (compare Haas, J., 1906, **59**, 570; Dunstan and Carr, P., 1896, **12**, 48): a 2-metre tube charged with lead chromate gave satisfactory results (Found : N = 16·18, 16·22. $C_{13}H_{17}O_3N_3$ requires N = 15·97%). The substance was soluble in alcohol or hot benzene, slightly soluble in hot acetone, insoluble in other solvents. Yield about 13%.

Methyl o-*Aminobenzoate and Benzophenonesemicarbazone.*—Molecular quantities were heated at 210° for 40 minutes; ammonia was evolved and methyl alcohol distilled over. The melt on extraction with boiling benzene gave a residue which was shown by treatment with hot pyridine to consist of a little hydrazodicarbonamide and tetrahydroquinazoline-2 : 3-dione. Concentration of the benzene extract gave a mixture, from which 3-*diphenylmethylene-aminotetrahydroquinazoline-2 : 4-dione* was isolated by fractionally precipitating a chloroform solution with light petroleum. Concentration of these mother-liquors gave benzophenonecarbohydr-azone. Further concentration of the benzene extract yielded a little diphenyl ketazine.

3-*Diphenylmethyleneaminotetrahydroquinazoline-2 : 4-dione* crystallised from alcohol in large prisms, m. p. 240°, and was moderately soluble in hot chloroform or hot pyridine, insoluble in ether (Found : N = 12·32, 12·54. $C_{21}H_{15}O_2N_3$ requires N = 12·31%). Boiling for ½ hour with 2½N-hydrochloric acid effected hydrolysis into benzophenone and 3-aminotetrahydroquinazoline-2 : 4-dione. Kunckell obtained the hydrochloride from the base and alcoholic hydrogen chloride; evidently aqueous acid did not produce this salt.

If the reaction product is worked up in the usual way with acetic acid, the 3-amino-compound is obtained and not the benzophenone derivative.

Methyl o-*Aminobenzoate and Acetonesemicarbazone.*—Equimolecular quantities, heated at 195° for 30—40 minutes, gave ammonia and a distillate containing methyl alcohol and dimethyl ketazine;

water, acetone, or hydrazine was not present. A white sublimate, very small in amount and probably ammonium carbamate, gradually formed and the melt ultimately solidified; it was then extracted with a little boiling benzene to remove resinous matter and unchanged ester. The residue was washed with light petroleum and fractionally recrystallised from pyridine, which dissolved it completely, indicating absence of hydrazodicarbonamide. The first crop of crystals consisted of 3-aminotetrahydroquinazoline-2 : 4-dione, concentration yielded large, regular, efflorescent prisms, almost complete evaporation gave tetrahydroquinazoline-2 : 4-dione. The prisms, after recrystallisation from pyridine, charred at 390° on slow heating but melted at 420° in a previously heated bath (sodium-potassium nitrates). This substance, which could not be identified, contained about 32% of pyridine of crystallisation which was expelled at 105°; analysis then gave : $C = 60.32$; $H = 4.00$; $N = 17.41$; O (by diff.) $= 18.27$. The amount of this compound was relatively small; it was insoluble in the usual solvents, including hydrochloric acid, soluble in pyridine or sodium hydroxide. The solution in concentrated sulphuric acid became pink on standing.

3-iso*Propylideneaminotetrahydroquinazoline*-2 : 4-*dione*, obtained by boiling the 3-amino-compound with ordinary undried acetone until completely dissolved (5 hours), crystallised from dry acetone in prisms, m. p. 212° (Found : $N = 19.55$, 19.58. $C_{11}H_{11}O_2N_3$ requires $N = 19.35\%$). It was soluble in the usual organic solvents except ether and light petroleum; crystals from benzene were efflorescent, containing apparently solvent of crystallisation. A mixture of this substance with acetonesemicarbazone, on heating at 190° for 35 minutes, melted at first and then gradually solidified, ammonia was evolved, and dimethyl ketazine distilled in quantity. The solid, after removal of tarry matter by washing with ether and benzene, was identified as 3-aminotetrahydroquinazoline-2 : 4-dione : the evolution of ammonia was probably due to a decomposition of the semicarbazone, which gives this gas on heating.

The various substances mentioned were fully characterised as such by their properties and, if necessary, by analysis and preparation of derivatives.

XIX.—*Banded Bituminous Coal. Studies in the Composition of Coal.*

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON
WHEELER.

As the result of an investigation into the chemical nature of the
ingredients of banded bituminous coal (J., 1919, 115, 619), it was
found that the chief differences between them were expressed by a
regular gradation in composition and in properties which could be
accounted for by assuming the occurrence in each, in different
proportions, of " reactive " and " inert " types of compounds.
We are now able to offer as the result of later work, more particularly
that on dopplerite (J., 1922, 121, 2345), an explanation as to the
character of these presumed " reactive " and " inert " constituents.

The various plant entities and residues that have contributed
to the formation of the organic substance of coal can conveniently
be grouped according as they are :

(1) *Resistant to decay.*   Amongst the more important members
of this group are : (*a*) Spore-exines and cuticular tissues; and
(*b*) resins.

(2) *Subject to decay.*   The members of this group are either :
(*a*) Organised, such as cellulosic and lignified tissues; or (*b*) amor-
phous, the contents of plant cells.

(3) *The products of decay.*   The ulmins.

An accumulation of plant remains immediately after de-
position consists mainly of the first two groups, but in an older
deposit, such as a peat bed, certain changes have taken place.
The members of group 1 are still present in an apparently unaltered
form.   The cellulose and lignin of group 2, however, have suffered
decay, undergoing such minor alterations as dehydration produces,
or becoming ulmified (probably in conjunction with certain of the
cell-contents), or disappearing altogether.   According to Fischer
and Schrader (*Brennstoff Chem.*, 1921, 2, 23), the lignin alone sur-
vives in any form, the cellulose of necessity vanishing (being con-
verted into liquid and gaseous products through the agency of
bacteria), but we cannot regard this view as either proved or prob-
able, and consider that ulmins can be produced from any plant
material of carbohydrate type.   Judging from the nature of peat,
ulmification is the main chemical process during the decay of plants
and it proceeds further the older the deposit : thus, whilst a young
peat may yield only 10 or 20% of material soluble in alkalis, from
an older peat as much as 70 or 80% can be extracted.

In a deposit of the age of coal, it cannot be expected that the

materials of any of the three groups will remain unaltered.   Spore-
exines and cuticular tissues may not be much changed, nor need
the resins, but the cellulose that is not totally destroyed will in
large part be converted, together with the more resistant lignin
and part of the cell-contents, into the amorphous ulmins of group 3
(or products derived from them).   There will also be material corre-
sponding with group 2 (a), consisting of altered (but apparently
not ulmified) woody tissues, such as compose many lignites and
are recognisable in many bituminous coals.   We have at present
no knowledge as to what becomes of the non-ulmified portions
of the cell-contents.   As they finally appear in the coal, cell-wall
structures, group 2 (a), may not differ much chemically from the
amorphous ulmins, but the materials of group 1 differ markedly.

The more recent beds of plant remains, the peats, contain a large
amount of alkali-soluble material, the amount increasing with the
age of the deposit : but " older " fuels, such as brown coals and
lignites, contain comparatively little, whilst bituminous coals,
unless they have been considerably weathered, usually contain
none.   This diminishing content of alkali-soluble material, after
a certain stage has been passed, would seem to be due to a change
in the character of the ulmins, through condensation, dehydration
and loss of carboxyl (with the formation of anhydrides and lactones)
whereby their usual property of dissolving in alkalis to form dark
brown solutions is lost.   The alkali-soluble ulmins that surround
and permeate the plant structures in an old peat (see J., 1922, **121**,
2345) may be presumed to have their counterpart in bituminous
coal in the amorphous cementing material (insoluble in alkalis)
in which the numerous plant structures are embedded.

We have already (loc. cit., p. 2354) instituted a comparison and
shown the similarity between dopplerite, a typical peat ulmin
which occurs segregated in bands in some peat bogs, and vitrain,
the brilliant structureless ingredient of banded bituminous coal.
By analogy, there should also be a close relationship between all
the amorphous cementing material of bituminous coal, whether
segregated, as in a vitrain, or diffused, as in a clarain and a durain,
and the amorphous ulmins that form so large a part of the older
peats, and this relationship should extend to the amounts of amor-
phous material normally contained in the two fuels.

The correctness of this suggestion can be deduced from the data
obtained during the study of the chemical nature of the ingredients
of banded bituminous coal, referred to at the beginning of this
paper.

The " reactivity " of the vitrain, clarain, and durain of Hamstead
coal, as measured by their susceptibility to attack by solvents

and reagents and by the amounts of liquid and gaseous products
yielded on destructive distillation, was found to diminish in the
ratio 1·0 : 0·9 : 0·7, taking the ingredients in the order named,
and it was concluded that the amounts of " reactive " material
they contained diminished in the same proportion.   Of the absolute
amounts of " reactive " and " inert " materials present in any one
of the ingredients, no conclusion could be drawn at the time the
experiments were made, but with the recognition of vitrain as related
to the nearly homogeneous ulmin, dopplerite, it follows that the
bulk of vitrain should be regarded as " reactive."

Whence, since its composition had been found to be similar in
all three ingredients, it must be concluded that the reactive material
of a clarain and a durain is essentially an insoluble derivative of
the ulmins and that in the clarain and durain of Hamstead coal
it is present to the extent of about 90 and 70%, respectively.
Actually, the vitrain contained a certain amount of material other
than insoluble ulmins (resins, for example), so that these figures
should be reduced somewhat.

It is difficult to judge from an examination of transparent sections
of coal as to the proportions of amorphous and organised material
present, but even if, as appeared, there is in the Hamstead durain,
for example, a greater proportion of plant tissues than the 30%
indicated by calculation, there are grounds for the belief that some
plant remains in coal (woody tissues in particular), although they
retain their organised structures, have been partially ulmified and
thus function as " reactive " material.   Otherwise, the plant
entities (especially those of group 1) must constitute what we have
termed the " inert " material of coal.

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XX.—*The Oxidation of Banded Bituminous Coal at Low Temperatures.   Studies in the Composition of Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

OF the methods that have been used for studying the chemical
composition of coal, attack by reagents has not, in general, yielded
much information.   The majority of the reagents used have been
oxidants, such as nitric acid or Schultze's solution, and these either
yield intractable gelatinous substances—the ulmins and their
substitution products—or, ultimately, fatty acids, usually oxalic

acid.   The use of a milder oxidant, such as atmospheric air at low temperatures, enables progressive changes in the character of the coal-substance to be studied, and, apart from the importance that a study of the oxidation of coal by air has in relation to its spontaneous combustion, many of the observations made throw light on the character of some of the ingredients of coal and thus help towards an understanding of its constitution.

The atmospheric oxidation or "weathering" of coal has been found to increase the proportion of substances extractable by alkaline solutions—the ulmin compounds—or even to produce such substances where apparently none existed previously.   For example, Dennstedt and Bunz (*Z. angew. Chem.*, 1908, **25**, 1825), by heating a number of finely-powdered coals in open vessels during several days at 130—150°, showed that the effect of oxidation was, in some instances, to produce as much as 30 to 36% of ulmin compounds.   Mahler (*Ann. Mines*, 1913, **4**, 163) passed a slow stream of air during long periods through coal heated at low temperatures and found that traces of formic acid, methyl alcohol and acetone, and larger quantities of acetic acid, were present in the condensed products of oxidation, whilst the coals themselves became increasingly soluble in aqueous potassium hydroxide and their temperatures of initial decomposition decreased as oxidation proceeded.   If the temperature at which oxidation was effected was higher than 250°, the ulmin compounds (soluble in potassium hydroxide) formed at lower temperatures began to decompose.

The present research has as its object the tracing of the changes that take place in the character and composition of the coal conglomerate as oxidation slowly proceeds; and, more particularly, the comparison of the behaviour of the macroscopically distinct ingredients, into which most bituminous coals can readily be separated, when subjected to similar treatment.   For, inasmuch as these banded ingredients, which Stopes has provisionally named vitrain, clarain, durain and fusain (*Proc. Roy. Soc.*, 1919, *B*, **90**, 470), have been shown to possess markedly different chemical characteristics even when taken from contiguous portions of the same lump of coal (see Tideswell and Wheeler, J., 1919, **115**, 619; Baranov and Francis, *Fuel*, 1922, **1**, 219), an intimate study of the chemistry of " coal " must of necessity treat of each ingredient separately; whilst a comparison of the differences that exist between the ingredients which together form the coal as it occurs in nature throws light on the manner of its formation.

The coal chosen for this work was from the Top Hard seam at the East Kirkby Colliery, Nottinghamshire, a detailed examination of which has been recorded by Baranov and Francis (*loc. cit.*).

The vitrain, clarain, and durain bands in this coal are sharply differentiated, and it contains a fair proportion of fusain. No experiments were made with the clarain portion, since previous work led us to believe that the results would be intermediate between those for the vitrain and durain portions. The method of experiment was, briefly, to draw a slow current of moist air through weighed samples (50 g.) of the three ingredients in the form of powder (through a 60's and on a 90's sieve) contained in glass tubes which could be maintained at a constant temperature during prolonged periods. After passing through the coal, the air bubbled into a measured volume of cold distilled water to condense any liquid or soluble gaseous products. At stated intervals this water was examined and changed and a small fraction (5 g.) of each coal was removed from the tubes for analysis.

Oxidation at 100°.

Liquid and Gaseous Products.—The treatment of the coals with air at 100° was carried out in four stages, the first of two months' and the remainder each of 1 month's duration. The distilled water through which the air bubbled after leaving the coals had, in each instance, acquired a milky appearance * by the end of the first period and had increased in volume. Tests were made for alkalinity or acidity, formaldehyde, acetone, acetaldehyde, and methyl and ethyl alcohols. The chief results, expressed approximately as percentages on the coals, are recorded in Table I.

TABLE I.

		Period I (two months).	Period II (one month).	Period III (one month).	Period IV (one month).
Vitrain	Formaldehyde	0·007	0·017	0·007	nil
	Methyl alcohol	0·014	0·006	nil	,,
	Acids	0·040	0·006	trace	,,
Durain	Formaldehyde	0·002	0·010	nil	,,
	Methyl alcohol	0·014	0·002	,,	,,
	Acids	0·004	trace	trace	,,
Fusain	Formaldehyde	nil	0·010	nil	,,
	Methyl alcohol	,,	0·004	,,	,,
	Acids	,,	trace	trace	,,

None of the solutions contained acetone or acetaldehyde, nor could any trace of ethyl alcohol be detected. The acids appeared to be either formic or acetic acid; sulphurous acid, which might have been derived from pyrites or sulphur compounds in the coals, was absent, nor was the acidity due to carbon dioxide in solution. The production of formaldehyde and methyl alcohol was not

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* This was found to be due to bacterial growths, presumably derived from the coals; it disappeared during subsequent periods of the oxidation.

continuous, the liquids in the wash-bottles after the fourth oxidation period remaining apparently pure water; we believe that they were produced from methane occluded in the coals, probably by the action of ozone formed as the air bubbled through the wash-bottles leading to the coal samples.

Changes in the Coal Substance during Oxidation.—The examination of the samples withdrawn at each period during the oxidation included proximate analyses, of the usual type and by means of solvents, and ultimate analyses. The results are summarised in Tables II, III, and IV.

TABLE II.

Proximate Analyses.   Oxidation at 100°.

		Original	Period I.	Period II.	Period III.	Period IV.
Vitrain	Moisture %	9·58	0·02	0·08	0·71	0·98
	Ash %	1·14	1·37	1·56	1·78	1·76
	Volatile matter (% on ash-free dry coal)	30·74	31·01	30·69	31·16	31·06
	Calorific value (cals. per g.)	7949	6969	6515	6348	6266
Durain	Moisture %	3·58	0·02	0·35	0·93	0·78
	Ash %	4·05	4·06	3·95	3·80	3·95
	Volatile matter (% on ash-free dry coal)	28·91	26·55	25·00	27·08	27·04
	Calorific value (cals. per g.)	7465	6973	6697	6530	6515
Fusain	Moisture %	1·66	0·10	0·32	0·92	0·90
	Ash %	17·78	17·57	17·76	17·80	17·96
	Volatile matter (% on ash-free dry coal)	19·84	23·69	22·27	20·98	20·78
	Calorific value (cals. per g.)	6466	5978	5891	5770	5750

The original moisture in the coals was driven off during the first period of oxidation and thereafter each ingredient showed an increasing tendency to retain water or to absorb it rapidly from the air, behaviour characteristic of coals that are naturally of high oxygen-content.   The results of the " volatile matter " determinations indicate differences in the character of the oxidation of the different portions of the same seam of coal, the fusain and the durain presenting a peculiar contrast.   The fusain showed an increase in the amount of volatile matter after the first period of oxidation, but the amount diminished as oxidation proceeded, assuming a nearly constant value higher than that of the original material; whilst with the durain there was a marked decrease at first and then a gradual increase to a constant value less than that of the original coal.   With vitrain the values remained constant within the limits of experimental error, with perhaps a tendency towards a slight increase.   The vitrain was the only one of the three

ingredients that coked strongly before oxidation and its coking-power was destroyed after the first period of heating. It will be noticed that the vitrain suffered the greatest depreciation in calorific value.

TABLE III.

Analyses by Solvents.   Oxidation at 100°.

		Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	α-Compounds	79·7%	85·6%	85·4%	87·6%	87·6%
	β-Compounds	14·6	10·4	11·0	9·6	9·9
	γ-Compounds	5·7	4·0	3·6	2·8	2·5
	Ulmins	0·02	11·17	11·25	11·3	11·2
Durain	α-Compounds	90·5	90·0	90·0	87·9	87·6
	β-Compounds	6·8	7·05	—	9·2	9·4
	γ-Compounds	2·7	2·95	—	2·9	3·0
	Ulmins	0·01	2·6	5·58	6·6	6·52
Fusain	α-Compounds	95·2	95·20	96·54	95·0	94·15
	β-Compounds	3·4	3·35	—	3·5	4·45
	γ-Compounds	1·4	1·45	—	1·5	1·40
	Ulmins	nil	1·2	1·8	1·7	2·2

For convenience the nomenclature proposed by Stopes and Wheeler (" The Constitution of Coal," H.M. Stationery Office, 1918), which makes no presumptions as to the nature of the fractions obtained by means of solvents, has been employed, " α-compounds " signifying that portion of coal insoluble in pyridine at its boiling point, " β-compounds " that portion soluble in pyridine but insoluble in chloroform, and " γ-compounds " that portion soluble both in pyridine and chloroform.*   The term " ulmins " signifies those compounds in the coal as a whole that were soluble in alcoholic potassium hydroxide.

The most striking changes on oxidation have occurred with the vitrain.   Soluble ulmins were formed rapidly, the change by oxidation at 100° being apparently complete at the end of the first period of heating, and simultaneously about 30% of both the β- and γ-compounds (amounting to 6% of the coal) was destroyed.   The β-compounds obtained from the original coal formed a chocolate-brown powder, whilst those from the oxidised coal appeared as brown nodules of dried jelly similar to the ulmins.   It seemed probable, therefore, that the β-compounds from the oxidised vitrain contained a relatively large proportion of the ulmins.   The quantities of material available from this series of experiments did not permit of testing this assumption directly, but it was found that the 87·6% of α-compounds only contained about half the ulmins produced.

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* The α-, β-, and γ-compounds as thus defined are not necessarily similar in character in the oxidised and unoxidised coals.

The 9·9% of β-compounds recorded as being present in the oxidised coal must therefore be regarded as largely ulmified.

With both the durain and the fusain the changes on oxidation were not so great as with the vitrain, smaller amounts of ulmins were produced, and there was a tendency for the amounts of β-compounds (probably ulmified) to increase as oxidation proceeded.

TABLE IV.

Ultimate Analyses.   Oxidation at 100°.

(Expressed as percentages on the ash-free dry substances.)

		Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	Carbon	79·7	74·3	72·2	71·9	72·1
	Hydrogen	5·2	4·1	3·9	3·8	3·8
	Oxygen	12·1	18·6	21·2	21·3	21·1
	Nitrogen	1·7	1·6	1·6	1·8	1·8
	Sulphur	1·3	1·4	1·1	1·2	1·2
Durain	Carbon	81·7	77·6	76·1	76·1	76·5
	Hydrogen	4·8	3·9	3·7	3·6	3·7
	Oxygen	11·3	16·3	17·8	17·8	17·1
	Nitrogen	1·6	1·4	1·4	1·4	1·5
	Sulphur	0·6	0·8	1·0	1·1	1·2
Fusain	Carbon	85·9	83·1	81·3	81·1	81·1
	Hydrogen	3·9	3·5	3·2	3·3	3·3
	Oxygen	8·4	11·6	13·6	14·1	13·8
	Nitrogen	1·3	1·2	1·3	1·0	1·2
	Sulphur	0·5	0·6	0·6	0·5	0·6

Analyses of α-*Compounds.*

		Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	Carbon	78·0	73·2	73·2	71·7	71·6
	Hydrogen	4·8	4·1	3·8	3·5	3·6
	Oxygen, etc.	17·2	22·7	23·0	24·8	24·8
Durain	Carbon	81·5	75·5	75·9	75·5	75·7
	Hydrogen	4·5	3·7	3·7	3·4	3·3
	Oxygen, etc.	14·0	20·8	20·4	21·1	21·0
Fusain	Carbon	86·9	83·5	82·2	81·4	81·2
	Hydrogen	3·8	3·4	3·2	3·1	3·2
	Oxygen, etc.	9·3	13·1	14·6	15·5	15·6

The vitrain, durain, and fusain from the original coal used showed the same gradations in analysis as were found by Tideswell and Wheeler for the Hamstead coal. During oxidation there was an increase of between 5 and 10% in the oxygen contents of each ingredient and a corresponding decrease in the carbon and hydrogen contents. With the vitrain, since the proportion of α-compounds increased markedly on oxidation, there was a tendency for their ultimate composition to approach that of the oxidised coal.

The proportions of nitrogen and sulphur did not vary outside the limits of experimental error, but the nature of the sulphur-

compounds present altered, as is shown by determinations of " sulphate " sulphur, as follows :

<div align="center">TABLE V.</div>

<div align="center">*Sulphur as Sulphates.*   Per cent.</div>

	Original.	Period I.	Period II.	Period III.	Period IV.
Vitrain	nil	0·18	0·15	0·15	0·14
Durain	,,	0·16	0·18	0·14	0·17
Fusain	,,	0·19	0·28	0·26	0·25

The sulphates were produced by the oxidation of pyrites originally present in the coal, the fusain being the ingredient that contained most pyrites.

A measure of the relative rates of oxidation of the three ingredients can be obtained from the percentage increase in the amount of oxygen present in the samples withdrawn at successive time-intervals. The results are shown in Fig. 1 as graphs which closely resemble those obtained in another manner by Tideswell and Wheeler for the rate of absorption of oxygen at 100° by vitrain, durain and fusain from Hamstead coal (J., 1920, **117**, 798, Fig. 3).
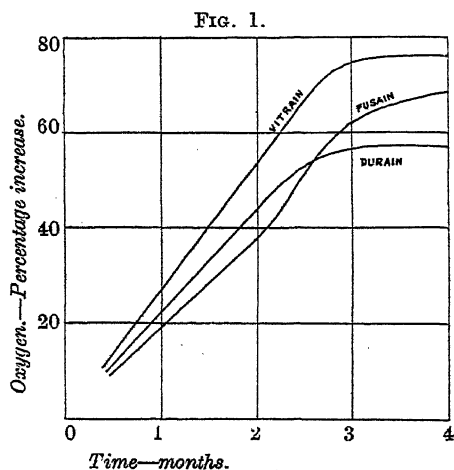
FIG. 1.

Oxidation at 150°.

It was assumed that at the end of 5 months' treatment the action of oxygen on the coals at 100° was complete, an assumption warranted by the analytical data so far as the vitrain is concerned, but perhaps not quite correct with respect to the durain, which as a whole was more resistant to attack. The remainder of each sample that had been oxidised at 100° during 5 months was now heated at 150° whilst moist air was drawn through. Heating was continued during 6 months, samples of the coals being withdrawn at intervals of 2 months and the liquids in the wash-bottles examined.

Liquid and Gaseous Products.—The wash-bottle connected to the fusain sample contained only a solution of carbon dioxide, but after each period of heating the solutions from the vitrain and durain samples were markedly acid (sulphurous acid) and contained

formaldehyde.   The presence of acetone or methyl alcohol could not be detected.

Changes in Weight.—During oxidation at 100° the weight of each coal had at first increased slightly and then decreased, the final values being : vitrain + 0·8, durain − 1·3, and fusain − 1·4% on the original weight.   Oxidation at 150° resulted in a progressive decrease in weight, as is shown in Table V.

TABLE V.

Loss in weight on oxidation at 150°.   Per cent.

	Period I.	Period II.	Period III.	Total.
Vitrain	8·8	7·3	0·2	16·3
Durain	4·6	5·5	3·0	13·1
Fusain	3·3	4·4	0·8	8·5

Changes in the Coal Substance.—The changes that took place in the character of the coals during oxidation at 150° are best appreciated by comparing the analytical data with those recorded for the final samples oxidised at 100°.   Each coal showed a marked increase in the amount of " volatile matter " and an increase in ash-content occasioned by the loss in weight of combustible matter. These results are recorded in Table VI.

TABLE VI.

Proximate Analyses.   Oxidation at 150°.

		Final oxidation at 100°.	Period I.	Period II.	Period III.
Volatile matter % on ash-free dry substance	Vitrain	31·0	40·7	40·4	40·5
	Durain	27·0	31·8	32·1	32·2
	Fusain	20·8	25·9	25·9	27·1
Ash %	Vitrain	1·76	2·22	2·15	2·17
	Durain	3·95	4·73	4·86	4·95
	Fusain	17·96	17·98	17·90	18·25

The most remarkable result of the oxidation at 150° was that the vitrain was rendered nearly completely soluble in alcoholic potassium hydroxide (compare Charpy and Decorps, *Compt. rend.*, 1921, **175**, 807), whilst the durain and fusain also contained greatly increased quantities of ulmins.   The quantities, together with the results of analysis by means of pyridine and chloroform, are recorded in Table VII.

It has been seen that oxidation at 100° tended to destroy the compounds soluble in pyridine, and to a less degree those soluble both in pyridine and chloroform.   Further oxidation at 150° apparently destroyed the γ-compounds completely, or at all events rendered them insoluble in chloroform ; at the same time larger

TABLE VII.

Analyses by Solvents.   Oxidation at 150°.

		Final oxidation.	Period I.	Period II.	Period III.
Vitrain	α-Compounds	87·6	75·9	57·7	55·0
	β-Compounds	9·9	23·2	42·3	45·0
	γ-Compounds	2·5	0·9	trace	nil
	Ulmins	11·2	93·5	97·0	95·5
Durain	α-Compounds	87·6	87·4	80·3	77·0
	β-Compounds	9·4	12·1	19·7	23·0
	γ-Compounds	3·0	0·5	trace	nil
	Ulmins	6·5	36·1	43·5	46·0
Fusain	α-Compounds	94·2	94·5	82·0	80·0
	β-Compounds	4·5	5·5	18·0	20·0
	γ-Compounds	1·3	trace	trace	nil
	Ulmins	2·2	14·2	19·5	24·0

proportions of the coals were rendered soluble in pyridine.   It is doubtful, however, whether with these oxidised coals the degree of solubility in pyridine is of much significance, since prolonged exposure of the coals to pyridine results in further extraction.

TABLE VIII.

Ultimate Analyses.   Oxidation at 150°.

(Expressed as percentages on the ash-free dry substances.)

		Final oxidation at 100°.	Period I.	Period II.	Period III.
Vitrain	Carbon	72·1	66·4	64·7	64·9
	Hydrogen	3·8	2·7	2·5	2·3
	Oxygen, etc.	24·1	30·9	32·8	32·8
Durain	Carbon	76·5	71·9	68·9	67·0
	Hydrogen	3·7	2·5	2·6	2·3
	Oxygen, etc.	19·8	25·6	28·5	30·7
Fusain	Carbon	81·1	77·8	73·9	74·2
	Hydrogen	3·3	2·4	2·3	2·2
	Oxygen, etc.	15·6	19·8	23·8	23·6

Analyses of α-Compounds.

			Period I.	Period II.	Period III.
Vitrain	Carbon	71·6	67·7	65·9	64·9
	Hydrogen	3·6	3·1	2·7	2·3
	Oxygen, etc.	24·8	29·2	31·4	32·8
Durain	Carbon	75·7	73·1	69·9	—
	Hydrogen	3·3	2·8	2·9	—
	Oxygen, etc.	21·0	24·1	27·2	—
Fusain	Carbon	81·2	78·2	77·0	75·2
	Hydrogen	3·2	2·5	2·5	2·3
	Oxygen, etc.	15·6	19·3	20·5	22·5

Ultimate analyses were also made of some of the samples of ulmins produced on oxidation at 150°, as follows :

		Carbon.	Hydrogen.	Oxygen, etc.
From vitrain.	Period I.	64·8	2·8	32·4
From vitrain.	Period II.	64·5	2·7	32·8
From vitrain.	Period III.	64·6	2·6	32·8
From durain.	Period III.	65·4	3·0	31·6

All these ulmins have similar analyses and the similarity extends to ulmins produced from the coals by oxidants other than air, to which reference will be made later. With vitrain, which was completely ulmified by oxidation at 150°, the analysis of the coal as a whole and that of the a-compounds contained in it were also similar. Thirty or more analyses of the fully oxidised vitrain have shown between 62 and 66% of carbon and between 2·6 and 3·5% of hydrogen. Some of these observed slight differences in analysis may be accounted for by the fact that the ulmins are unstable compounds and suffer slight decomposition, with elimination of water, on prolonged heating at 150°.

It is apparent that marked changes have taken place in the coals during oxidation at 150°. With vitrain, almost the whole of the coal substance has been converted into alkali-soluble ulmins, whilst large proportions of both the durain and the fusain have been so converted. It is to this ulmin formation that the changes in the proximate and ultimate analyses, and in the general character of the coals, are due. The ultimate analyses show that the carbon content of the vitrain reached a minimum value owing to its almost complete conversion into alkali-soluble ulmins, whilst the corresponding values for the durain and the fusain are higher because of the presence of substances more resistant to such ulmification or perhaps incapable of it.

Oxidation at 200°.

Oxidation was continued at a higher temperature to find out whether complete ulmification of the durain and fusian would occur and to determine what changes, if any, would take place in the vitrain. The remaining portions of the samples heated at 150° were oxidised at 200° during 1 month and examined. Each ingredient had lost about 25% in weight during this treatment, with a corresponding increase in its percentage of ash. A final period of oxidation during a fortnight was then carried out. Analytical data are recorded in Table IX.

Further ulmification of the durain had occurred, but was by no means complete, nor did it appear that more prolonged heating, or heating at a higher temperature, would be satisfactory, for decomposition of the oxygenated coals (with the production of carbon dioxide and carbon monoxide) was taking place fairly rapidly. The ulmins produced from the vitrain at 150° began to decompose (as is shown by the ultimate analyses) and were rendered partly

TABLE IX.

Oxidation at 200°.

	Vitrain.		Durain.		Fusain.	
	Period I.	Period II.	Period I.	Period II.	Period I.	Period II.
Loss in weight %	27·0	7·2	23·5	7·4	19·7	7·0
Ash %	2·8	2·8	6·4	6·5	21·4	21·5
Volatile matter (% on ash-free dry substance)	38·5	39·0	37·8	37·1	29·8	31·2
Ulmins	70·0	75·0	64·0	65·0	20·5	22·0
Soluble in pyridine	28·0	30·0	22·0	24·0	11·0	13·0
Carbon ⎧ % on ash-free	65·8	65·9	69·8	70·0	72·8	71·3
Hydrogen ⎨ dry sub-	2·0	2·01	1·8	1·76	1·8	1·6
Oxygen, etc. ⎩ stance	32·2	32·09	28·4	28·24	25·4	27·1

insoluble in alcoholic potassium hydroxide; indeed the solutions obtained were unlike those of the true ulmins, being turbid and lacking the rich brown colour. So far as the vitrain is concerned, the production of alkali-soluble ulmins must be regarded as having been completed by oxidation at 150°.

By carefully regulated oxidation it has thus been found possible to obtain from all the ingredients of the coal examined ulmins having similar analyses and properties and presumably derived from substances of the same nature that occur in different proportions in each ingredient. The vitrain consists almost entirely of these "reactive" compounds, the durain contains a certain proportion of relatively "inert" substances, and the fusain a greater proportion.

These conclusions bear out and amplify the suggestion made by Tideswell and Wheeler (*loc. cit.*, p. 633) that the difference, chemically, between the vitrain, clarain, durain and fusain of a banded bituminous coal lies in the proportion of relatively "inert" or unresponsive material with which the "reactive" portion is associated, the "reactive" group of compounds being of the same chemical nature in each ingredient and containing more oxygen and less carbon than the "inert" material, which may differ in character as between one ingredient and another. The present research specifies as the "reactive" group of compounds those that can be converted by oxidation into alkali-soluble ulmins. The "inert" substances are those that remain after a durain or a clarain has suffered all the ulmification possible by oxidation, and it would appear that they impart to the coal most of the specific qualities it may possess. For examination of the residue from the durain after ulmification had been completed showed that it consisted essentially of the plant entities (chiefly spore-exines) that, originally resistant to the processes (bacterial and other) that resulted in the formation of the coal conglomerate, still remained resistant to oxidation.

This process of formation of alkali-soluble ulmins by oxidation (more properly, a process of regeneration) thus affords means, which we have long sought, of effecting a separation of the different plant entities from the coal mass and examining their chemical properties, according to the scheme outlined by Stopes and Wheeler (" The Constitution of Coal," H.M. Stationery Office, p. 41). The process of oxidation by air at 150° is a long one and only admits of the treatment of small quantities of coal. We therefore made comparative experiments with other oxidants the action of which could be regulated and found in hydrogen peroxide a reagent which, if carefully used, would rapidly effect the complete transformation of a vitrain into alkali-soluble ulmins and, whilst rendering the bulk of a clarain or a durain soluble, would leave their characteristic plant tissues substantially unaltered. The analysis of ulmins prepared by the action of hydrogen peroxide on coal averages : carbon 64·3, hydrogen 3·5, and oxygen 31·2%, which is in close agreement with that of the similar compounds produced by slow atmospheric oxidation at 150°.

We have spoken of the formation of alkali-soluble ulmins from bituminous coal as a " regeneration." The solubility of the ulmin-compounds in alkaline solutions to form dark brown liquors is usually regarded as one of their chief characteristics and this property is used for their estimation. From estimations made in this way it is found that the various groups of alkali-soluble ulmin-compounds form a large proportion of the " humus " of decayed wood; they occur, sometimes in considerable quantities, in peats; lignites also contain them, but in normal bituminous coals they occur rarely, and then only in minute quantities, whilst in anthracites their presence has never been detected. In other words, the further the natural " carbonisation " of the fuel has progressed the smaller is its content of soluble ulmins. From this it is probable that the ulmin compounds once formed during the early processes of formation of the fuels have been subsequently so modified as to render them unrecognisable by their solubility in alkalis. Berthelot and André (*Ann. Chim. Phys.*, 1892, (vi], **25**, 420) observed that both ulmins formed artificially from sugar and those occurring naturally in soil began to decompose on exposure to air when moist, carbon dioxide being evolved; Roger and Vulquin (*Compt. rend.*, 1908, **147**, 1404) made a similar observation on peat ulmins and noted also that they became insoluble in alkalis; whilst Tideswell and Wheeler have recorded in their study of dopplerite (J., 1922, **121**, 2345) that this undoubted ulmin is less readily soluble in alkalis than that in more recent peats. Solubility in alkalis to form brown solutions should not, therefore, be regarded as a necessary property of the

ulmins, but it must be recognised that they can (through polymeris-ation and dehydration) change in character so as to lose their " characteristic " solubility.

Neither the insoluble ulmins, which we consider form the major part of newly-won bituminous coals, nor the soluble ulmins regener-ated from them by oxidation are identical in character with those that form the major part of peat, but they possess the same nuclear structure. The external groupings of the ulmin molecules in unoxidised coal are modified during oxidation, the more easily detached groupings being eliminated to form simple oxygenated compounds, whilst the residual ulmin becomes more definitely of acidic character (more so than the peat ulmins) owing to the form-ation of carboxylic groupings in place of those detached. Pearson (*Fuel*, 1924, **3**, 297) has reached similar conclusions to these as the result of his work on the oxidation of coals by sulphuric acid and bromine, although the analyses of the ulmins so formed differ from ours (obtained either by atmospheric oxidation or by the use of hydrogen peroxide), no doubt because chemical changes other than oxidation occurred during his experiments.

Bituminous coal, then, consists essentially of insoluble ulmins in which morphologically organised plant tissues (that have escaped ulmification) are dispersed.* The present work shows that alkali-soluble ulmins can be regenerated from a bituminous coal by mild oxidation. If the coal is a vitrain, it consists almost solely of ulmins; whilst the regeneration of alkali-soluble ulmins in a clarain, a durain, or a fusain leaves residues, characteristic of each of those ingredients, which are essentially the original plant entities that were particularly resistant to, or were preserved from, the processes of " decay " that constituted the early stages of coal-formation, and are, apparently, but little altered.

The character of these residues is illustrated in Fig. 2, in which (*a*) and (*b*) are photomicrographs of cuticular tissues such as can be separated from a clarain by treatment with hydrogen peroxide and alcoholic potassium hydroxide, (*c*) shows the exine of a megaspore, characteristic of the *débris* from a durain, obtained in the same manner, and (*d*) a wood tracheid such as occurs in the *débris* of a fusain. Future communications will deal with the chemical

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* For the sake of simplicity, we have here omitted discussion of the presence of natural plant-substances devoid of morphological organisation, such as " resin," in the coal conglomerate. We have evidence that these resist oxidation at low temperatures and appear amongst the plant *débris* after the process of regeneration of alkali-soluble ulmins by means of hydrogen peroxide (or atmospheric oxidation). This work will be described in a forth-coming publication which deals also with the chemical properties of the regenerated ulmins.

FIG. 2.
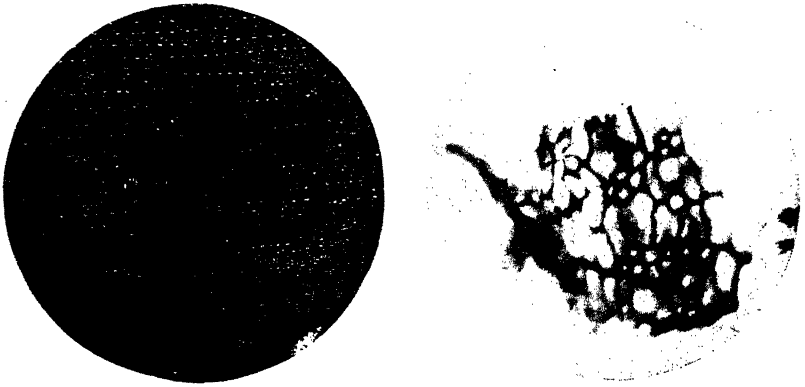
(a) and (b).   Fragments of cuticular tissue, characteristic plant entities
in a clarain.   (a × 30 and b × 180.)

(c) and (d).   The exine of a megaspore (× 30) and a wood tracheid (× 250),
characteristic plant entities in a durain and a fusain respectively.

examination of similar plant-tissues separated in bulk from coal; in particular with cuticles and spore-exines, since these are so often the predominant structures to be found in clarains and durains, respectively, and most bituminous coals consist mainly of clarain and durain. Work on modern cuticles and spore-exines, for comparison, has already been in progress some years in the belief, now justified, that it should be possible to isolate individual tissues or identifiable parts from coal so that, for example, any characteristic distillation products of which they are the source can be determined.

DEPARTMENT OF FUEL TECHNOLOGY,
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XXI.—On Fusain and its Oxidation. Studies in the Composition of Coal.

By FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER.

SPONTANEOUS combustion in a seam of coal, in so far as it may be determined by the chemical composition of the materials composing the seam, originates with the most readily oxidisable ingredient thereof. Amongst mining men there is a belief, the history of which it is unnecessary to trace, that a frequent cause of spontaneous combustion is the presence in the seam of fusain; * that fire actually originates in bands of fusain, when such are present, and travels preferentially along them.

Data regarding the rate of oxidation of a fusain have been supplied by Winmill (*Trans. Inst. Min. Eng.*, 1913, 46, 563), who concluded that of all parts of the Barnsley seam, which he examined in detail, the fusain was the least capable of heating spontaneously. Our own experiments when using coal from the Hamstead Thick seam (J., 1920, 117, 794) gave quite different results. The vitrain, clarain and durain (the brilliant, bright and dull portions of the seam) absorbed oxygen at rates graded in the direction expected from previous work on the chemical constitution of these ingredients of banded bituminous coal (J., 1919, 115, 619), but the fusain stood apart. At 15° and 50° its absorptive power for oxygen was several times greater than that of the rest of the coal, although at 100° it was of the same order. From this it can be concluded that the fusain, weight for weight, is the most liable to self-heat (from

* Sometimes called "mother of coal," "mineral charcoal," "dant," or "sooty partings."

atmospheric temperature) of all the ingredients of the Hamstead coal. It would not, however, be justifiable to assume that fusains from other coals behave similarly—Winmill's work, indeed, suggests that they do not—and further experiments with a number of samples of fusain and of the coals associated with them were therefore undertaken.

During the progress of this work, which was begun in 1919, determinations of the rates of oxidation of a number of fusains from different coal-fields have been published by Graham (*Trans. Inst. Min. Eng.*, 1923, **66**, 41), who has summarised his results as follows : " This ingredient of coal may vary very considerably in composition, but such variation does not appear, at low temperatures, to affect materially the absorption of oxygen which in all cases is considerably smaller than that shown by a bituminous coal liable to spontaneous combustion. In general, from the chemical point of view fusain may be exonerated from being considered as the source of the main production of heat during the initial stages of most cases of spontaneous combustion."

The following results may be quoted from Graham's work, the oxygen absorbed being expressed in c.c. at $N.T.P.$ per gram of fusain :

Fusain description.		Oxygen absorbed from air at 30° during 96 hours. C.c.
Mossfield seam	(North Staffs.)	1·93
Seven Foot seam	(North Staffs.) {(a) Soft variety	1·19
	(b) Hard variety	2·04
South Wales {(a) Soft variety		1·87
(b) Hard variety		1·61

The absorption of oxygen by the actual coals with which the fusains were associated was not measured, but Graham compared his results with some obtained by Winmill (*ibid.*, 1916, **51**, 493), under similar conditions of experiment, for coals " liable to spontaneous combustion," the values for which lay between 3·0 and 6·0 c.c. A closer scrutiny of Winmill's figures shows, however, that coal from the same fields as those from which Graham's fusains were obtained did not absorb oxygen any more readily, and Graham's generalisation does not seem to us justifiable on the evidence.

We have measured the absorption of oxygen of a number of coals and of the fusains actually associated with each, and we cannot agree that fusains in general absorb oxygen at slower rates than do coals liable to spontaneous combustion.

Seventeen samples of fusain, with samples of the adjoining coals, were collected for us by H.M. Inspectors of Mines and from these four were chosen, according to their apparent purity, for oxidation tests.

The samples were as follows :—

Lab. No. A. From Top Hards, Barnsley Seam, Hucknall No. 2 Pit, Notts.

Lab. No. B. From Robin's Seam, Cannock Old Coppice Colliery, Walsall, Staffs.

Lab. No. C. From Deep Softs Seam, Mapperley Colliery, Notts.

Lab. No. D. From Dysart Main Colliery, Fife.

Analytical data respecting these samples are given in Table I.

TABLE I.

	A.		B.		C.		D.	
	Fusain.	Coal.	Fusain.	Coal.	Fusain.	Coal.	Fusain.	Coal.
Moisture, per cent. ...	5·6	9·4	5·6	8·9	2·6	9·8	5·7	10·9
Volatile matter (other than moisture) ...	15·7	39·0	17·1	39·8	13·0	40·4	12·3	35·9
Ash	10·3	3·3	14·7	8·3	12·5	7·7	11·8	1·3
Carbon, per cent. (on ash-free dry coal)	89·4	79·1	79·8	73·5	87·5	75·6	84·6	78·5
Hydrogen	3·0	5·0	3·3	4·8	3·0	4·7	3·2	4·6
Oxygen	7·0	12·8	6·1	15·3	6·4	16·5	10·5	15·1
Nitrogen	0·4	2·2	0·4	1·5	0·7	1·9	0·4	1·3
Sulphur	0·2	0·9	10·4	4·9	2·4	1·3	1·3	0·5

FIG. 1.
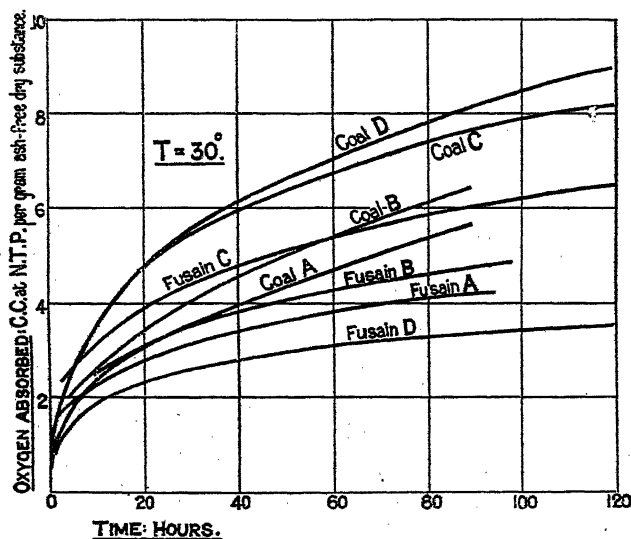
The method of experiment was to circulate oxygen in a closed system through the coal or fusain packed in a tube maintained at a constant temperature.* The absorption of oxygen was calculated

* Details of the apparatus used and of the method of experiment are given in J., 1920, **117**, 795, whilst a diagram of a similar apparatus is shown in J., 1912, **101**, 831.

from the reduction of pressure. Before and after oxidation at a given temperature, each sample was heated in a vacuum at 200°. The results obtained are shown diagrammatically in Figs. 1 and 2 and are summarised in Tables II and III.

These results cannot be directly compared with those of Graham, for he used air in his experiments, but Winmill has found (*Trans. Inst. Min. Eng.*, 1916, **51**, 493) that the absorption of oxygen by coal is nearly proportional to the square root of its concentration,

FIG. 2.
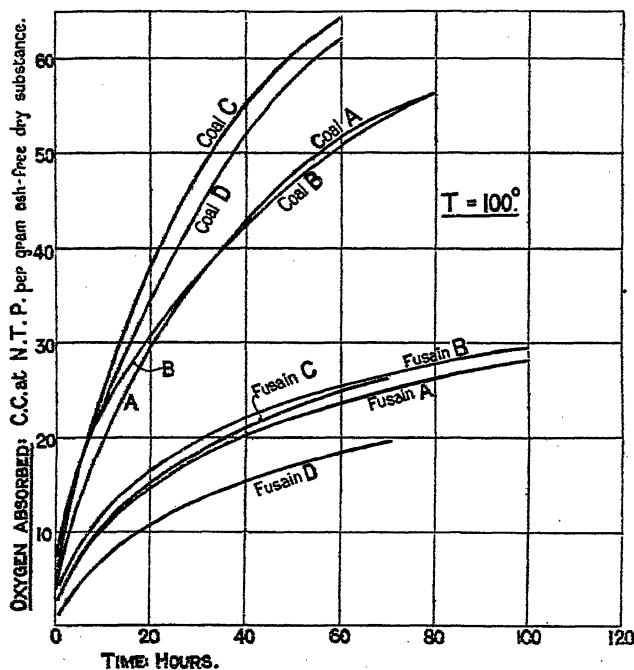
TABLE II.

Oxygen absorbed. C.c. at N.T.P. per gram of ash-free dry substance.

		Sample.						
		A.		B.		C.		D.
Temp.	Time (hours).	Fusain.	Coal.	Fusain.	Coal.	Fusain.	Coal.	Fusain.	Coal.
30°	1	1·3	1·0	1·4	1·2	1·8	1·5	0·8	1·4
	10	2·3	2·4	2·5	2·6	3·2	3·8	1·8	3·8
	50	3·5	4·3	4·0	5·0	5·1	6·4	2·9	6·7
	96	4·3	5·8	4·8	6·6	6·2	8·1	3·5	8·5
100°	10	10·5	19·2	12·2	22·4	11·0	25·0	7·2	23·8
	50	22·0	48·0	24·0	47·0	22·8	61·0	17·0	59·0

TABLE III.

Ratio : Oxygen absorbed by fusain : Oxygen absorbed by coal.

Temp.	Time (hours).	A.	B.	C.	D.
	1	1·3	1·2	1·2	0·6
30°	10	0·95	0·96	0·84	0·47
	50	0·83	0·81	0·80	0·43
	96	0·74	0·73	0·76	0·41
100°	10	0·55	0·55	0·44	0·30
	50	0·46	0·48	0·38	0·28

so that a rough comparison can be made if Graham's figures are doubled. It then appears that the fusains he used were decidedly less readily oxidised at 30° than most of those we have investigated. We suggest that this is due in part to the different experimental methods used (Graham, for example, does not appear to have allowed for the oxidation of his samples at atmospheric temperature previous to their introduction into his apparatus), but mainly to differences in the nature of the fusains themselves. The abnormally low rate of oxidation of the Barnsley fusain recorded by Winmill would appear to be due to weathering of the sample previous to his tests.

It will be seen from Tables II and III that with three of the pairs of samples examined the initial absorption of oxygen by the fusain at 30° was greater than that by the coal, but on comparing the results obtained at 30° and 100°, the oxidisability of fusain is found to increase less rapidly with temperature than that of the coal. The temperature coefficients of the amounts of oxygen absorbed during the early stages (up to 10 hours) are :

	A.	B.	C.	D.	Hamstead.
Fusain	1·24	1·27	1·12	1·29	1·20
Coal	1·34	1·34	1·39	1·37	1·35

In each instance the coefficient is less than 2 and probably is the resultant of two coefficients. The reaction between oxygen and coal is not simple : it may be expressed as follows :

Coal and oxygen ⟶ coal-oxygen (adsorbed) ⟶ coal-oxygen (complex) ⟶ oxidised coal + oxides of carbon + water.

The last phase of the reaction is incomplete at low temperatures, but can be completed by raising the temperature (it is nearly complete at 200°) ; at such low temperatures absorption of oxygen is determined by the formation of the coal-oxygen complex. Compared with the rate of formation of this complex, the first action of adsorption may be regarded as instantaneous. The rate of complex formation will therefore depend on the concentration of oxygen on the surface of the coal. The temperature coefficient of the con-

centration of adsorbed oxygen on the surface of the coal is less than unity and is probably about 0·80 (see Graham, *Trans. Inst. Min. Eng.*, 1916, **52**, 338; Tideswell and Wheeler, J., 1919, **115**, 895). Assuming that the rate at which the coal-oxygen complex is formed is directly proportional to the concentration of the oxygen maintained on the surface of the coal and that its temperature coefficient is 2, the expected coefficient for the series of reactions would be 1·6. The observed values are less. An explanation of this is that the surface of the coal becomes clogged by the products of decomposition of the complex, an effect which would be greater the higher the temperature of reaction and more noticeable with fusain than with coal because of the more open texture of its surface.

A study of the gases evolved during the oxidations (see Table IV) suggests that the mode of oxidation of fusain and of coal is similar. At 30° the amount of carbon monoxide was too small to admit of exact determination, but at 100° the volumes were both larger and more regular in amount and it was found that the ratio between the carbon dioxide and carbon monoxide produced at this temperature lay within the same range (2·4 to 3·4) with the fusains as with the coals.

TABLE IV.

Oxides of carbon evolved. Per cent. of oxygen absorbed.

Temp.			Sample. A.	B.	C.	D.
30°	Carbon dioxide	Fusain	4·0	0·8	1·6	0·8
		Coal	1·5	3·2	5·6	0·7
100	Carbon dioxide	Fusain	12·8	11·7	10·8	14·5
		Coal	10·6	12·1	14·5	17·6
100	Carbon monoxide	Fusain	4·7	4·0	4·0	4·4
		Coal	4·0	4·9	6·2	5·2
	Ratio $\frac{CO_2}{CO}$	Fusain	2·7	2·9	2·7	3·3
		Coal	2·65	2·5	2·4	3·4

With none of the fusains examined was the rate of absorption of oxygen at low temperatures so rapid as with the Hamstead fusain, which may be regarded as exceptional. Fusain does not form an important part by weight (rarely more than 5%) of the mass of a coal, but it occurs frequently in patches or in layers of considerable extent, generally adjacent to or embedded in bright coal, and its porous nature allows of ready access of oxygen. Both its chemical properties and its physical state therefore enable it to produce the first local rise in temperature that may result in self-heating of the adjacent coal. Once the temperature has risen, the continuance of the heating is no doubt mainly due to oxidation of the coal.

It is not to be expected that all fusains, no matter from what seams of coal they are procured, should have similar chemical and physical properties, any more than that all coals should be similar.

We have, in fact, evidence from the work of Sinnatt (*Trans. Inst. Min. Eng.*, 1921, 62, 156) that in the Lancashire coal-fields there are at least two types, a dense and a pulverulent variety, whilst, as already mentioned, the Hamstead fusain with which we made our previous experiments seems to be of a particularly reactive character. We concluded from our work on banded bituminous coal (*loc. cit.*, p. 634) that the three principal ingredients of Hamstead coal, vitrain, clarain and durain, are each composed of a " reactive " group of compounds together with a relatively " inert " material, and differ from one another mainly in the proportions of these constituents contained in them. Although the fact was not emphasised at the time, the chemical examination of the Hamstead fusain showed that it also must be regarded as containing a certain proportion of " reactive " constituents, of similar type to those in the coal, which is responsible for many of its properties. Similarly, it would appear from Sinnatt's work and from our own observations that many, if not all, fusains consist of an intimate mixture of coaly material with an " inert," or true fusain, constituent.

The occurrence of fusain in coal seams is usually attributed to rapid aerial decay of the plants at or near the water surface of the swamps in which most of the *débris* was submerged, and the process most often appears to have taken effect on the woody parts of the plants. There is no reason why such aerial decomposition should always have been completed before the plants became submerged and anaerobic decomposition began; indeed it is more probable that in the majority of instances the aerial decay was not complete. Fusains may therefore be expected to differ from one another not only, occasionally, by reason of differences in the plant remains fusainised, but also, frequently, because the material has suffered in differing degree an in part aerobic and in part anaerobic decomposition, the latter resulting in ulmification. Lomax has, indeed, observed complete stems of plants that have been fusainised on the outside and consist of true coal within (*Trans. Inst. Min. Eng.*, 1921, 62, 171), but we suggest that each individual fusain fibre may often consist of an inner core of coaly material with an outer layer of true fusain, with, no doubt, intermediate zones merging the one into the other; and there may also be only partial fusainisation of some of the cell-walls composing the fibre.

The " true fusain " material appears to be quite insoluble in organic solvents; it yields mainly oxides of carbon and methane on distillation, with little or no liquid products, and consists usually of thickened and " carbonised " cell-walls. We consider that the intimate admixture of different proportions of oxidisable coaly material with this chemically " inert " but very porous true fusain

material mainly determines the different degrees of oxidisability of fusains as they exist in coal, the fusain in the Hamstead coal, for example, containing a high proportion of coaly material throughout its fibres. Support is lent to this view by analyses of a number of fusains made for us by Mr. A. E. Beet. These samples of fusain had been collected with great care and before they were subjected to analysis were examined closely for fragments of adhering coal. Yet it was found that each could be separated into two distinct classes of material by sieving through a 40's mesh. The fraction which remained on the sieve was associated with much coaly material, to judge by the results of analysis (more particularly distillation tests at 900°), though it could not be recognised as coal; whilst that which passed through was, on the same evidence, mainly what we have termed "true fusain" material.

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XXII.—*The Chemistry of Lignin. Part II. A Comparison of Lignins Derived from Various Woods.*

By WALTER JAMES POWELL and HENRY WHITTAKER.

IN Part I of this series (J., 1924, **125**, 357), the preparation and properties of lignin derived from flax shoves and of several of its derivatives were described. The chief conclusions drawn were that the empirical formula for flax lignin which agrees most closely with all the analytical data is $C_{45}H_{48}O_{16}$, and that the molecule contains one active aldehyde group and nine hydroxyl groups, of which four are methylated. The investigation has now been extended on the same lines to lignins obtained from a number of woods, and poplar, birch, ash, spruce, larch and pine lignins, together with some derivatives of these substances, have been examined. The wood lignins were isolated in the same way as flax lignin, the wood in the form of small chips being digested for 6 to 10 hours under pressure at temperatures varying from 140° to 160° with caustic soda solution, the strength of which varied from 8 to 12%. The black liquor was drained from the cellulose and treated while still hot with a slight excess of hydrochloric acid, the precipitated lignin being washed by decantation with hot dilute hydrochloric acid, centrifuged and dried. An objection might be raised that this method of isolation would cause internal changes to take place in the lignin molecule. Lignosulphonic acid, however,

has been obtained from spruce wood by Dorée and Hall (*J. Soc. Chem. Ind.*, 1924, **43**, 257T) by a mild process—the action of a 7% solution of sulphurous acid at 100—110°—and the composition of this substance corresponds with the formula $C_{26}H_{30}O_{12}S$, from which the formula $C_{26}H_{28}O_9$ for lignin is obtained. This requires $C = 64 \cdot 4$, $H = 5 \cdot 9\%$; and these figures are in close agreement with our results (Table I). Our product is therefore not more highly condensed than that of Dorée and Hall, and both are probably closely related to lignin as it exists in the lignocellulose complex.

The crude lignin was purified by pouring the solution in aqueous acetone into a large volume of hot 20% hydrochloric acid, the precipitate being collected and thoroughly washed with hot water.

The results now obtained show conclusively that the lignins from the different natural sources so far examined are derivatives of the same hydroxy-compound, and that they differ only in the number of methoxyl groups which they contain. This difference is mainly due to the fact that the methoxyl content of lignin in wood varies from one species to another, while in any one species variations occur according to the age of the tree. In addition, the methoxyl content of lignin isolated in the manner already described is affected by the strength of caustic soda solution and the time and temperature of digestion. Lignin as isolated is therefore a mixture of methylated derivatives of a polyhydroxy-compound, and it should be possible by chemical means to effect separation into fractions of definite methoxyl content, but our attempts to do so have not yet met with success. The separate fractions obtained by precipitating lignin from its solution in caustic soda by addition of hydrochloric acid gave the same figures on analysis.

In deducing the formula $C_{45}H_{48}O_{16}$ from the analytical results given by flax lignin and its derivatives, the assumption was made that the molecule contained a definite number of methoxyl groups, whereas in our present view there is no reason to suppose that such is the case. Instead of the total of nine hydroxyl groups indicated by analysis of acetyl-lignin, it is possible to suggest formulæ containing eight or ten hydroxyl groups (*e.g.*, $C_{40}H_{44}O_{14}$) which agree equally well with the analytical data. At this stage of the work, however, it is not desirable to make a decision in favour of one or the other of these formulæ and until more data are available we intend to continue using the formula adopted for flax lignin, $C_{45}H_{48}O_{16}$.

From the six wood lignins, purified as described above, the acetyl compounds were prepared by treatment on the steam-bath with acetic anhydride and sulphuric acid. The acetyl content varied according to the methoxyl content, but in each case, using the

empirical formula $C_{45}H_{48}O_{16}$ as the basis of calculation, the total of acetylated and methylated hydroxyl groups was nine, although the actual number of methylated groups varied between three and five. All the acetyl compounds were insoluble in cold alkali and it is therefore unlikely that there are any carboxyl groups in the molecule. The variations in methoxyl content of the various wood lignins prepared were not sufficient to affect the determinations of carbon and hydrogen which were carried out on the purified samples, and the figures obtained were constant within the limits of experimental error. Table I gives a summary of the analytical results and also the number of groups calculated on the basis of the formula $C_{41}H_{40}O_{16}$ for the parent hydroxyl compound itself. It is proposed to assign the name *lignol* to this compound.

TABLE I.

Substance analysed.	Determination.	Source of Lignin.						
		Flax.	Larch.	Pine.	Spruce.	Ash.	Birch.	Poplar.
Lignin.	C	63·9	63·8	63·4	64·0	63·2	63·2	63·3
	H	5·8	5·2	5·6	5·5	5·6	5·5	5·8
	CHO	3·1	—	2·9	3·1	—	3·2	—
Acetyl-lignin.	OMe	11·8	9·0	11·5	11·0	13·3	15·2	12·6
	CO·CH₃	20·5	23·0	18·9	19·4	17·6	14·5	17·5
No. of OMe groups.		4·0	3·1	3·9	3·8	4·5	5·0	4·3
No. of CO·CH₃ groups.		5·0	5·8	4·5	4·8	4·3	3·4	4·3
Total groups.		9·0	8·9	8·4	8·6	8·8	8·4	8·6
Acetylmethyl-lignin.	OMe	20·3	19·9	20·4	23·1	20·0	22·4	22·7
	CO·CH₃	11·1	11·8	10·5	8·0	11·3	8·1	7·5
No. of OMe groups.		6·5	6·4	6·5	7·2	6·4	7·0	7·0
No. of CO·CH₃ groups.		2·6	2·7	2·4	1·8	2·6	1·8	1·7
Total groups.		9·1	9·1	8·9	9·0	9·0	8·8	8·7

The table shows that lignol from each of the wood lignins examined has the same empirical formula and the same number of hydroxyl groups as that from flax lignin. In order to verify this statement experimentally, attempts have been made to isolate lignol from the various lignins by the action of hydriodic acid. However, on treating lignin with hydriodic acid (d 1·7) at 130°, a dark brown product, which appeared to be a mixture, was obtained. The main fraction of this product was insoluble in caustic soda and cannot therefore be lignol, and as the percentage of carbon found is much higher than that calculated, it appears that reduction takes place during the reaction with hydriodic acid.

Confirmation of the results and conclusions drawn from the analysis of the acetylated lignins was obtained by examination of the methylated derivatives. The latter were prepared by treatment of the sodium hydroxide solution of lignin with methyl sulphate in the cold. It is not possible to methylate more than seven of the hydroxyl groups under the conditions employed, and

in some cases full methylation was obtained only after several treatments.   The product from a single treatment, however, after being washed with dilute sodium hydroxide solution, was acetylated in the usual manner, and the total of methoxyl and acetyl groups in all the products was found to be practically constant.   It was stated in the paper on flax lignin (*loc. cit.*) that the proportion of acetyl in acetylmethyl-lignin was too low to account for the presence of two acetyl groups.   In the experiments on which this statement was based, acetic anhydride alone was used as the acetylating agent, but it has since been found that in presence of sulphuric acid the diacetyl derivative is readily formed.   The analytical data given in Table I for the acetylmethyl-lignins strongly support the view that all the various lignins examined have the same empirical composition and number of hydroxyl groups in the molecule.

Derivatives of an entirely different character from those already described result when lignin is treated with chlorine or bromine, and if there were any fundamental differences in the molecular structure of the various lignins, it is unlikely that the same halogenated derivative would be obtained in each case.   In our study of flax lignin we found that the chlorination or bromination product contained twelve halogen atoms, and that a large quantity of hydrogen chloride or bromide was evolved during halogenation. Most of the methoxyl groups originally present in the lignin were removed, chlorolignin apparently containing two, and bromolignin containing only one, methoxyl group.   Six of the twelve chlorine atoms in flax chlorolignin were eliminated with great ease, for example, by dissolving the fully chlorinated derivative in cold dilute sodium hydroxide, the hexachlorolignin being precipitated on acidification.   Hexachlorolignin contains only one methoxyl group and therefore the fully chlorinated product, dodecachlorolignin, can contain only one such group, and is similar to the bromocompound in that respect.   The higher figure for methoxyl obtained on analysis is due to the ease with which hydrogen chloride is eliminated during estimation in the Zeisel apparatus.   The Perkin method for the determination of acetyl also gives high results in the case of acetyldodecachlorolignin owing to the liberation of ethyl chloride.

The six wood lignins have been brominated and subsequently acetylated.   The dodecabromolignins and their acetyl derivatives on analysis gave results agreeing closely with those obtained from the corresponding products derived from flax lignin (Table II). The dodecachlorolignins prepared from two wood lignins were similar in composition to flax dodecachlorolignin.   A mixture of

the six wood dodecachlorolignins, on solution in dilute sodium hydroxide solution and reprecipitation with hydrochloric acid, gave a product comparable in all respects with flax hexachlorolignin. It may also be noted that the various acetylated dodecachlorolignins were more readily hydrolysed than the corresponding bromo-compounds, a behaviour similar to that of the derivatives from flax lignin, and that in all cases both acetyl derivatives were insoluble in cold sodium hydroxide solution.

A third type of derivative, nitrolignin, has been prepared from each wood lignin, and the products were identical with that from flax lignin in composition, three nitro-groups having been introduced into the molecule. As in the case of flax nitrolignin, a part of the nitrogen is present as organic nitrate, as is evident by the fact that a proportion can be estimated by the Lunge or Schultze-Tremann method. The total nitrogen, however, can only be determined by the Dumas or Kjeldahl method. The nitration of lignin proceeds equally readily whether nitric acid alone (40%) or a mixture of nitric and sulphuric acids is used, the products containing the same percentage of nitrogen. These facts indicate the probability of the presence of aromatic nuclei in lignin. Acetylnitrolignin is soluble in cold alkalis, and it is possible that nitrolignin contains one or more carboxyl groups. In this connexion it may be noted that elementary analysis of the nitro-compounds shows that some oxidation has taken place in addition to nitration. Owing to the ready hydrolysis of the acetylnitrolignins, it is difficult to deduce the number of hydroxyl groups in the molecule from analyses of this compound.

TABLE II.

Substance analysed.	Determination.	Flax.	Larch.	Pine.	Spruce.	Ash.	Birch.	Poplar.
					Source of Lignin.			
Dodecabromo-lignin	C	28·0	28·2	—	—	28·1	—	—
	H	1·5	1·6	—	—	1·6	—	—
	Br	55·2	55·0	54·8	55·2	55·1	54·7	54·9
Acetyldodeca-bromolignin	OMe	1·8	1·6	—	—	—	2·4	2·1
	CO·CH₃	9·4	9·8	9·0	9·8	—	—	9·2
Dodecachloro-lignin	Cl	35·1	35·5	—	—	—	36·0	—
	OMe	5·2	4·9	—	—	—	5·1	—
Nitrolignin	C	50·4	50·2	—	50·6			
	H	3·8	3·8	—	3·9			
	N	4·2	4·1	4·1	—	4·3	—	4·2
	OMe	3·0	3·2	2·6	3·1	3·0	3·3	—
Hexachloro-lignin	C	50·1			49·5*			
	H	3·0			3·2*			
	OMe	3·45			3·5*			
	Cl	20·8			20·4*			
Methyl-lignin-phenylhydrazone	N	—			7·5*			

Samples prepared from a mixture of equal quantities of the wood lignins.

Some discussion has recently taken place in the literature as to whether or not lignin evolves furfuraldehyde on distillation with 12% hydrochloric acid, and in view of this we have carefully examined our products, using the volumetric method for the estimation of pentosans in wood cellulose previously described by us (*J. Soc. Chem. Ind.*, 1924, **43**, 35T). Average results for the six crude lignins obtained by acidification of the alkaline liquor showed the presence of 0·9% of pentosans. This value was reduced to 0·3% by one purification from acetone and hydrochloric acid, whilst the product from a second purification gave no trace of furfuraldehyde. We therefore regard as untenable the view of Hägglund (*Cellulosechemie*, 1923, **4**, 73) that lignin contains 5% of furfural-yielding carbohydrate as an integral part of the molecule.

Of the sixteen oxygen atoms present in the molecule of lignin, nine are in the form of hydroxyl groups and one as an aldehyde group. The presence of the latter was indicated by measurements of the amount of Fehling's solution reduced by lignin, and was confirmed in the case of flax lignin, by a volumetric determination of the amount of phenylhydrazine required to form the phenyl-hydrazone. The following experiment shows, however, that the monohydrazone is only formed under the mild conditions used in the volumetric method, and that the reaction can be made to proceed further. Methyl-lignin was allowed to react with a hot alcoholic solution of phenylhydrazine, and the product freed from phenylhydrazine by several precipitations from acetone and hydrochloric acid. Analysis showed that three phenylhydrazine molecules had reacted with each molecule of lignin, and therefore that two ketonic groups must also be present. Methyl-lignin was used instead of lignin in order to avoid the formation of a phenyl-hydrazine ester. These results may be summarised by writing the formula for lignol in the extended form

$$C_{38}H_{30}O_4(CO)_2(CHO)(OH)_9.$$
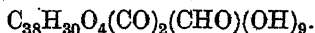
The details of the experimental work are similar to those given in Part I for flax lignin, and are therefore not repeated.

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XXIII.—A Redetermination of the Atomic Weight of Bromine. The Inseparability of the Isotopes by Fractional Crystallisation.

By PERCY LUCOCK ROBINSON and HENRY VINCENT AIRD BRISCOE.

THE only precise experimental evidence in support of the generally accepted view that isotopes are inseparable by fractional crystallisation is the attempt by Richards and Hall (*J. Amer. Chem. Soc.,* 1917, **39**, 531) to separate thus the isotopic forms present in lead derived from Australian carnotite. Both they and Soddy (J., 1911, **99**, 72; *J. Amer. Chem. Soc.,* 1917, **39**, 1614) refer to the earlier data, which need not be quoted here.

Richards and Hall obtained no evidence of separation by 904 effective crystallisations, but their lead presented a relatively unfavourable case, since it contained only about 20% of the heavier isotope and the nitrates of the isotopes differed in solubility by but 0·74% (Richards and Schumb, *J. Amer. Chem. Soc.,* 1918, **40**, 1403). Since Aston's work has disclosed the existence of isotopes of many of the lighter elements, it has become clear that cases may be found permitting a more precise test (or proof) of inseparability by fractional crystallisation. The isotopes of boron differ by 10% in atomic weight, but the isotope ratio is unfavourable (approximately 20% B^{10} and 80% B^{11}), and an accurate determination of the atomic weight is both difficult and laborious. A prolonged fractionation of boric acid was effected, but the determinations of atomic weight, although they had other unexpected features of interest (see following paper), proved valueless for the purpose now under discussion.

Bromine, in the form of ammonium bromide, seems to present the best test-case, because (1) bromine has but two isotopes (Br^{79} and Br^{81}), present in nearly equal proportions and differing by 2·2% in atomic weight, (2) hydrogen and nitrogen are " simple " elements and together form less than 20% of the salt, (3) the atomic weight of bromine can be determined by direct and trustworthy methods, and (4) ammonium bromide crystallises from water in a fashion convenient for a long series of fractionations.

Therefore, with the double object of making a re-determination of the atomic weight of bromine and of confirming, in this more favourable case, the finding of Richards and Hall, ammonium bromide was subjected to prolonged fractional crystallisation and the atomic weight of the bromine in the final head and tail fractions was determined by measurement of the ratio Ag : AgBr.

Purification of Reagents.

Water.—Laboratory distilled water, already free from halogen, was redistilled from a little caustic soda and potassium permanganate in a 10-gallon copper still through a vertical spray-trap packed with glass beads and condensed in pure tin. The first and last portions of the distillate were rejected and the main fraction was collected and stored (for but a short time) in 20-litre stoppered resistance glass bottles which had been well cleaned, steamed out and kept for months full of distilled water. Many nephelometric tests were made, but on no occasion did the water give any indication of chloride.

Ammonia.—Ammonia gas, liberated by warming the purest commercial ammonia ($d = 0.880$), was dissolved in pure water, in an apparatus constructed entirely of resistance glass with a ground-in leading tube.

Sulphur Dioxide.—The gas, used both for the conversion of bromine to hydrobromic acid and for the precipitation of silver by Stas's method, was always obtained from the middle fraction of a syphon of the liquid.

Nitric Acid.—Commercial nitric acid, containing only small traces of halogen, was thrice redistilled in an apparatus constructed of " Duro " resistance glass with ground joints, large head and tail fractions being rejected. The final main fraction, tested in the nephelometer, was free from halogens. It was kept in a resistance glass bottle having a well-ground glass stopper protected by a glass cap.

Formic Acid.—The purest obtainable reagent acid was twice redistilled from a fused silica flask having a ground-in silica condenser and adapter. Considerable head and tail fractions were rejected in each distillation, and the main fraction was preserved in a stoppered silica flask.

Magnesia.—Magnesium nitrate was thrice precipitated from saturated aqueous solution by excess of nitric acid, filtered on porcelain, dissolved in water, and precipitated with ammonia. The hydroxide was washed by decantation, filtered, dried at 100°, ignited in air in a platinum dish, and finally heated at about 1000° in a current of moist pure hydrogen. Magnesia boats, moulded from the pure oxide moistened with dilute nitric acid, were ignited and used on a silica plate.

Hydrochloric Acid.—Commercial reagent acid was freed from arsenic by treatment with a copper-tin couple and distillation from copper gauze according to the method of Thorne and Jeffers (*Analyst*, 1906, **31**, 101).

Zinc.—A sample of granulated electrolytic zinc, kindly supplied

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by Messrs. Brunner Mond & Co., Ltd., proved to be free from arsenic and was used without further purification.

Hydrogen.—This gas, prepared from pure hydrochloric acid, containing a little platinic chloride, and pure zinc in a Kipp's apparatus, passed to a purifying train, the several parts of which were sealed together, in which it traversed successively a 12 inch column of concentrated potassium hydroxide solution, two 12 inch columns packed with broken sticks of potassium hydroxide, and two 10 inch columns packed with phosphorus pentoxide distributed on glass wool.

Silver.—Two samples, "A" and "B," were used, prepared in the same way but at different times and from different samples of commercial silver nitrate. In each case a filtered aqueous solution of silver nitrate (200 g.) was precipitated in a volume of about 20 litres with ammonium bisulphite according to the method of Stas (Briscoe, J., 1915, **107**, 69). The precipitated silver was washed six times with dilute ammonia, allowed to stand over-night with ammonia, washed six times with water, and dried at 100°. This silver, in 100 g. portions, was dissolved in pure nitric acid, precipitated hot with ammonium formate in a bulk of 2 litres, well washed with ammonia and water, and dried, first at 100° and finally at 250°, in an electrically heated covered beaker.

Before weighing, the silver was melted on a boat of pure magnesia in an atmosphere of hydrogen in an electrically heated silica tube furnace. The hydrogen issuing from the furnace during melting contained no impurities detectable by Marsh's test or by smell. At the end of each fusion the silver was collected into large buttons by shaking the furnace and these, when cool, were etched with 1 : 1 nitric acid, well washed with water, heated at 250° for 12 hours, and cooled in a desiccator over solid potassium hydroxide.

The Determination of Weight.

All precise weighings were made on an Oertling balance constructed specially for this work, resembling in many respects the standard type known as "No. 7, S.W.," but with a beam of Firth's 36% nickel-steel having a low coefficient of expansion, pan-supports of special design, and a separate enclosure for the beam after the principle used by Manley (*Phil. Trans.*, 1910, **210**, *A*, 387). No proper situation giving constant temperature and freedom from vibration was available for the balance : it was used on an ordinary stout wooden table in a room subject to vibration and to considerable and rapid fluctuations of temperature. Even under these adverse conditions, it gave results sufficiently precise and consistent for this work, a remarkable performance which is undoubtedly

attributable to the special features of construction indicated above.

The sensitiveness of the balance increased very slightly with the load and during all the work here described was very nearly 100 scale divisions per milligram. In weighing by the method of oscillations, the zero could easily be determined to the nearest half-division and the apparent weight thus ascertained with an error not exceeding 0·00001 g. A set of gold-plated brass weights with platinum fractions by Oertling and a gold 5-mg. rider were used and were calibrated to ascertain the relative weights in air on three separate occasions before and during the weighings. The corrections applied to ascertain relative weights in a vacuum were calculated using the density of air at the temperature and pressure observed during the weighing and the densities 10·49 and 6·47 for silver and silver bromide, respectively. As relative weights only were desired and the inequality of the arms of the balance was very small and constant, all weighings were made directly. All were made in duplicate and many in triplicate : in no case did the values for the vacuum weight thus obtained differ by more than 0·00003 g., thus it seems probable that the mean values are in error by less than this amount.

Silver was weighed directly on the balance pan : silver bromide was weighed in a stoppered glass bottle against a tare of the same glass and of closely similar form, volume and weight which had been treated in all respects as the bottle.

The balance case contained solid caustic potash and a piece of pitchblende.

The Fractional Crystallisation of Ammonium Bromide.

As starting material, commercial ammonium bromide, puriss., was used. Prolonged exposure to the laboratory atmosphere and contact with glass inevitably introduce impurities compared with which those originally present are insignificant; hence no attempt was made to ascertain the nature and amount of the latter.

About 2500 g. of ammonium bromide were dissolved in hot water in such proportion that about one-half crystallised out on cooling. Each fraction was again fractionated in a similar manner until a series of 30 fractions had been built up. Thereafter the number of fractions was kept constant and fractionation was continued in the usual way, by crystallising the whole series, taking away the " head " (most soluble) mother-liquor to form part of a new fraction, transferring each of the other mother-liquors to the crystals of the next higher fraction, adding water to the crystals of the " tail " (least soluble) fraction, and again crystallising the whole series.

A detailed scheme of such a fractionation is given by Richards and Hall (*loc. cit.*).   In all, 80 crystallisations of the whole series were thus made * and the total number of crystallisations, including those involved in the establishment of the series, was approximately 2700.

Throughout the later part of the fractionation each fraction contained about 80 g. of ammonium bromide, of which one-half was transferred at each crystallisation. The fractions were contained in 200 c.c. conical flasks closed against dust by loose hollow glass stoppers : distilled water of good quality was used for all crystallisations.

At the end of the fractionation, the extreme end fractions, Nos. 42 and 72, were rejected and the ammonium bromide of Nos. 43, 57 and 71, the " tail," middle, and " head " fractions, respectively, was taken for the atomic weight determinations.

Purification of Bromine for Analysis.

The volatility of bromine and its liberation from a bromide by oxidation afford an unexceptionable means of separating it sharply from all elements other than chlorine and iodine.   It is therefore with these elements, which would tend to concentrate in the tail and head fractions respectively, that the scheme of purification is concerned.   At the same time, as it was important that the determinations on head and tail fractions should be strictly comparable, both had to receive identical treatment.

Bromine is usually purified from the other halogens by applying the facts that it liberates iodine from an iodide, and is itself liberated from a bromide by chlorine.   Whilst in ordinary analytical work the assumption that these reactions are complete and irreversible holds well enough, they are probably not so in fact (see, *e.g.*, Schuyten, *Chem. Ztg.*, 1908, 32, 619).   The methods usually adopted for the rigorous purification of bromine for atomic weight work (see, *e.g.*, Scott, J., 1900, 97, 614; Baxter, *J. Amer. Chem. Soc.*, 1906, 28, 1322) reject so great a proportion of the material in head and tail fractions (using " head " and " tail " here in a chemical sense) as to ensure elimination of the other halogens, but were for that reason inapplicable to the small quantities (50—60 g. of bromine in each fraction) available for purification in this case.

Therefore each fraction of ammonium bromide was evaporated to dryness, dried at 160°, and weighed.   A quantity of pure sodium carbonate, about 5% in excess of the calculated amount, dissolved in a small quantity of water, was added to the bromide and the

whole was again evaporated to dryness and fused at about 800° in platinum in an oxidising atmosphere. Thus any organic impurities were destroyed.

A solution of about 1 g. of potassium dichromate and 30 c.c. of concentrated sulphuric acid in 170 c.c. of water was boiled vigorously for 10 minutes to expel any possible trace of halogen, cooled, and used to dissolve the sodium bromide from the platinum dish. This solution was transferred to the flask A of the distillation apparatus shown in Fig. 1, heated and kept boiling for about 10 minutes whilst the column B, jacketed with cold water, acted as a reflux condenser so that the free bromine might react with any trace of iodide present. Then the cooling was discontinued and the solution boiled until the bromine had distilled over into a flask containing pure water cooled externally by ice. Finally this flask was removed so that steam passed uncondensed right through the apparatus and carried away any residual traces of free halogen. The quantity of potassium dichromate used was calculated to displace about 2% of the total bromine, and the procedure described evidently favoured the elimination therewith of any trace of iodine.

After cooling, the flask was detached from the apparatus and into it was introduced a further quantity of potassium dichromate (35—45 g.) calculated to displace about 95% of the total bromine originally present. Then A was refitted to the condenser, heated very slowly, at first using B as a reflux condenser and later distilling slowly over into a flask as already described. Thus a main fraction of bromine and bromine water was obtained under conditions favourable to the reaction of any trace of chlorine with the residual bromide in solution. As a check, this solution was in each case treated with an excess of potassium dichromate and distilled a third time : the liberation of 1—2 g. of bromine afforded satisfactory evidence that excess of bromide had been present during the distillation of the main fraction.

Tests made with the largest (middle) fraction showed that digestion with sodium oxalate was unsatisfactory as a means of conversion to sodium bromide, and that the quantities available were too small to permit a satisfactory distillation of aqueous hydrobromic acid. Therefore, in working up the end fractions of ammonium bromide, the main fraction of bromine from the first oxidation was converted directly to hydrobromic acid by the use of sulphur dioxide, and the acid was subjected to a second fractional oxidation with potassium dichromate as already described.

Thus it was possible to obtain in each final main fraction of the second series of oxidations about 90% of the bromine present in the original ammonium bromide. This bromine was collected in an

excess of pure dilute aqueous ammonia and the resulting ammoniacal solution of ammonium bromide was transferred to a carefully cleaned, stoppered, resistance glass bottle which was kept free from dust in a clean desiccator until required for analysis.

Method of Analysis.

To avoid the uncertainty attendant on drying and weighing ammonium bromide, the ratio chosen for measurement was that of silver to silver bromide. A dilute aqueous solution of silver nitrate, made from an accurately known weight of silver, was precipitated with a slight excess of ammonium bromide and the silver bromide was washed, collected, dried, and weighed.

FIG. 1.	FIG. 2.	FIG. 3.	FIG. 4.	FIG. 5.
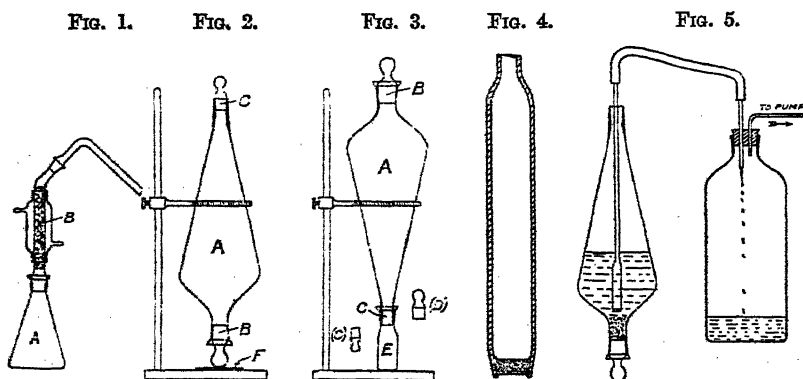
Platinum Gooch-Munroe crucibles were not available, so another method of collecting the precipitate was sought, and, as any transference is attended by risk of loss and is a source of doubt and anxiety, it seemed desirable, if possible, to collect and weigh the precipitate in the vessel in which it is formed but at the same time to avoid any weighing of large glass vessels. After several attempts, a satisfactory method was evolved whereby the precipitate was collected in a detachable part of a suitably shaped precipitation flask shown in Figs. 2 and 3.

A conical flask, A, of about 1700 c.c. capacity has two necks, B and C, fitted with hollow glass stoppers; the neck C has also an external taper, both this and the stopper D being ground into the neck of the weighing bottle, E. Four such flasks and two spare weighing bottles with stoppers, for use as tares, were made of "Durosil" glass, the joints and stoppers being very carefully ground and polished to an excellent fit : * the various parts of each set

* Our thanks are due to Mr. G. Ellison of this Department for his care and skill in executing this difficult task.

were etched with the same number. Before use the flasks and bottles were cleaned with chromic and nitric acids, washed, allowed to stand about three weeks containing a solution of ammonium bromide and nitric acid, allowed to soak for a further period in distilled water, and well washed.

In conducting a precipitation several buttons of pure silver, weighing about 4—5 g., were weighed, and dissolved in pure nitric acid in a solution flask of the form previously described (Briscoe, J., 1915, **107**, 78), and the solution was boiled to expel nitrous fumes, cooled, and diluted with pure water to about 400 c.c. Meanwhile, a measured volume of ammonium bromide solution, containing bromine about 5% in excess of that required by this silver, was acidified with pure nitric acid, diluted to about 700 c.c., and filtered into the precipitation flask supported by a padded ring and resting on a pad of filter paper, F, in the position shown in Fig. 2.

All succeeding operations up to and including the final weighings were conducted in orange light in a darkened laboratory set aside for this work. A rapid rotary movement was given to the bromide solution, the silver solution was poured into it with all the usual precautions to avoid loss, and 6—8 rinsings of the solution flask followed, bringing the total bulk in the precipitation flask to about 1400 c.c. Then the flask was stoppered and vigorously shaken, at first every 30 mins. and later about twice a day. After 7 days, the precipitate having become sufficiently dense and coherent for transference, the stopper C was removed and rinsed into the flask, and the supernatant liquor was syphoned off by means of the arrangement described later. By careful manipulation, the liquor left above the precipitate was reduced to 2—3 c.c.

Next the silver bromide was washed twice by decantation, using in each case about 1000 c.c. of wash-water, allowing the precipitate to settle 2—3 days, and syphoning off as in the first case. Commonly the precipitate tended to form a colloidal solution in the second wash, and a solution of about 0·5 g. of ammonium nitrate, prepared from pure ammonia and nitric acid, was added to avoid this difficulty.

Transference of the precipitate to the weighing bottle was effected by means of the second washing. The bottle, having been carefully heated in dry air, cooled, and weighed against the tare, was fitted to the flask at C and by reversing the whole apparatus into the position shown in Fig. 3 and alternately giving a rotary agitation and allowing the apparatus to stand, the silver bromide was washed down into E. Then the stopper B was removed, the wash-water syphoned off, the syphon tube and the walls of the flask were rinsed down with a fine jet of water, and the wash was syphoned off.

Finally the syphon was partly withdrawn, it and the flask were again rinsed, the bottle was detached, and the neck C rinsed into it.

The bottle containing the silver bromide with but 15—20 c.c. of water was then heated in an electrically heated sheet nickel air-bath, first at 85—90° until all free water had evaporated and then at about 250—300° for 12—14 hours. During the whole of this drying operation a current of air, supplied by a water-blast and dried by passing through a glass train over sulphuric acid, concentrated aqueous potassium hydroxide, and solid potassium hydroxide successively, was led into the bottle by a glass tube inserted through the lid of the oven. The tare was, of course, heated alongside the bottle and after cooling, usually for 3—4 hours in the current of dry air, both bottle and tare were stoppered, transferred to the balance case, and weighed. The heating and weighing were repeated once or twice to ensure that a constant weight had been attained.

In two of the preliminary experiments the silver bromide was afterwards fused in the bottle, heated in a small vertical electric furnace of silica provided with a window to allow observation of the fusion. As this treatment had no appreciable effect upon the apparent weight, it was omitted in the final analyses.

To minimise the risk of appreciable solvent action on the bottles, care was taken that they were never in contact with washings for more than 12 hours. There remains the risk of mechanical loss of glass from the ground joint; although Richards has shown that with a well made and carefully used joint this risk is small. Fortunately, satisfactory evidence that both these effects were negligible in the present work is afforded by comparing the weights of three of the bottles (weighed against the same tare) before and after the first series of precipitations :—

	Bottle I.	Bottle II.	Bottle III.
Apparent wt. before	2·02985	2·22330	3·22103
„ „ after	2·02987	2·22330	3·22104

Before the method above described was finally adopted, attempts were made to find a substitute for the Gooch-Munroe crucible which may be recorded briefly here. An alundum crucible was digested with 1 : 2 nitric acid for 6 hours and with repeated changes of water for 24 hours, washed thoroughly with water under suction, dried at 130° for 10 hours, and ignited to about 600° in a closed porcelain crucible. After cooling in a desiccator and standing on the balance pan for 30 minutes, the crucible had a weight of 12·47830 g. Then a litre of a clear filtered solution of 20 g. of ammonium bromide in 10% nitric acid was passed through the crucible, and it was washed and dried as before, when its weight was 12·47799 g. (loss 0·30 mg.). A repetition of the treatment reduced the weight to

12·47782 g. (loss 0·17 mg.) and a second repetition, using 5% nitric acid, caused a further change to 12·47746 g. (loss 0·36 mg.). Thus, evidently there was a continuous and variable loss too great to permit the successful use of alundum crucibles. A Jena filter crucible having a mat of sintered glass, similarly treated but dried for 14 hours at 350°, lost in weight 0·80 mg. : and among several such crucibles it was observed that the degree of fritting was not uniform, some mats being so friable that glass could be removed with the finger nail. Hence such crucibles, too, were dismissed as unsuitable.

The device used in syphoning the liquors and washings may here be described. Preliminary experiments showed that as the liquid level fell, fine particles of precipitate were apt to be dislodged from the sides of the flask and carried over with the washings. It was impracticable to reduce the syphon to a capillary fine enough to stop these particles, therefore, although the syphon was never brought in contact with the mass of the precipitate, some form of reverse filter was necessary. Disks of thin alundum or wads of spongy platinum fused into the ends of glass tubes proved much too slow, but a porous glass filter of the form shown in Fig. 4 proved satisfactory. It was made by taking powdered Durosil glass passing a sieve of 100 meshes to the linear inch and retained on a 200 mesh sieve, cleaning the powder by boiling with hydrochloric acid and washing with water, packing it wet to form a 3 mm. layer in the end of a 12 mm. bore Durosil tube, and then drying at 100° and heating carefully in a luminous flame until the glass sintered to a strong, coherent yet porous mass adhering firmly to the tube. After experience had been gained, it was possible thus to make filters which would pass 1000—1500 c.c. of water per hour with a pressure difference of 30—40 cm. of mercury and yet retain the finest particles of suspended matter.

Each filter was fused to a long tube and then carefully cleaned and soaked. In use it was connected by a length of clean pure rubber pressure-tubing to a clean bottle in which the liquors were received in the manner shown in Fig. 5.

In each analysis the first mother-liquor was tested to ensure that an excess of bromide had been used : as nephelometric tests gave in them no indication of silver, they were rejected. Some small particles of silver bromide adhered to the inner surface of the precipitation flask or were retained by the glass filter : therefore one filter was kept for each analysis and after the bottle and precipitate had been removed, the flask was stoppered at B and re-inverted, and a small quantity of pure ammonia was passed in the reverse direction through the filter, shaken round the walls of the flask and, with the rinsings of filter and flask, made up to a definite bulk.

The silver content of this solution and of the main washings was then determined by nephelometric comparison of aliquot portions with standard silver solutions, and the weight of silver lost thus ascertained · was deducted from the weight of silver originally taken.

Statement and Discussion of Results.

Several preliminary analyses, made on the middle fraction of ammonium bromide, No. 57, whilst useful in establishing the methods, are not comparable in value with those of the final series : hence the results are omitted here.

The final series consisted of eight determinations, four on the ammonium bromide from the head fraction No. 71 and four on that from the tail fraction No. 43. The essential data are given in Table I.

TABLE I.

Number of analysis.	Fraction of bromine.	Sample of silver.	Vacuum wt. (g.) of silver taken.	Silver (g.) lost in washings, etc.	Corrected vacuum wt. of silver.	Vacuum wt. (g.) of silver bromide.	Ratio Ag/AgBr.	Atomic weight of bromine.	Difference from mean.
Series I.									
1	71	A	3·69325	0·00058	3·69267	6·42874	0·574400	79·933	+0·019
2	,,	,,	5·06115	0·00297	5·05818	8·80494	0·574471	79·910	—0·004
3	,,	,,	3·93515	0·00374	3·93141	6·84337	0·574484	79·906	—0·008
4	,,	,,	3·67332	0·00097	3·67235	6·39249	0·574479	79·908	—0·006
				Mean of Series I.			0·574459	79·914	±0·009
Series II.									
5	43	A	5·14730	0·00146	5·14584	8·95708	0·574499	79·901	—0·015
6	,,	,,	3·08140	0·00111	3·08029	5·36261	0·574401	79·933	+0·017
7	,,	B	3·34631	0·00072	3·34559	5·82369	0·574479	79·907	—0·009
8	,,	,,	3·43817	0·00251	3·43566	5·98102	0·574427	79·916	+0·002
				Mean of Series II.			0·574451	79·914	±0·011
				General mean			0·574455	79·914	±0·010

In the first group of analyses the extreme variation in the ratio Ag : AgBr is 0·000084 or 1 part in 6840 : that in the atomic weight of bromine is 0·027 or 1 part in 2960. In the second group the corresponding variations are 0·000096 or 1 part in 5984 and 0·032 or 1 part in 2493. The magnitude and sign of these variations indicate that the mean value of the atomic weight deduced from each series has an error probably less than 0·01 or, in round numbers, about 1 part in 8000. The mean atomic weights from the two series differ by but 1 part in 40,000 : as a change of 1% in the isotope ratio would change the atomic weight by 0·02 and should have been appreciable in these determinations, it appears that a fractionation of ammonium bromide involving 2700 crystallisations does not produce such a change.

This result, affording as it does more precise confirmation of the

conclusion drawn by Richards and Hall, is of some theoretical interest. It is, in particular, instructive to institute a comparison between the present results and those recorded for salts of kindred rare-earths, where the solubility differences are of the same order.

The solubilities of the hexahydrated nitrates of lanthanum and neodymium, $La(NO_3)_3,6H_2O$ and $Nd(NO_3)_3,6H_2O$, are respectively, 151·1 and 152·9 parts of anhydrous nitrate in 100 parts of water (James and Whittemore, *J. Amer. Chem. Soc.*, 1912, **34**, 1168; James and Robinson, *ibid.*, 1913, **35**, 754). As the molecular weights are 324·8 (La = 138·8) and 330·2 (Nd = 144·2), the *molecular solubilities* are 0·46520 and 0·46515. The coincidence of these numbers within one part in 9000 is obviously accidental, but the molecular solubilities evidently differ by no more than the error of the solubility determinations, say 2 or 3 parts in 1000 parts.

The effect of fractional crystallisation in this case is shown in the investigations, *inter alios*, of Demarçay (*Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1021) and of Baxter and Chapin (*J. Amer. Chem. Soc.*, 1911, **33**, 1). In the latter case, for example, about 1600 crystallisations as double ammonium nitrates and about 1300 as simple nitrates produced a number of fractions of neodymium free from appreciable traces of other earths.

The fact that 2000 crystallisations or fewer completely separate these earths whilst more than 2500 crystallisations do not appreciably change the proportions of the two kinds of molecule in ammonium bromide may be explained by, and therefore affords chemical evidence supporting, the theories of Bohr and of Bury (*J. Amer. Chem. Soc.*, 1921, **43**, 1602) whereby the additional electrons in the atom of the heavier of a pair of rare-earth metals are supposed to be less intimately associated with the corresponding protons than are the additional electrons in the heavier of a pair of isotopes.

Regarding the data as one series of determinations of the atomic weight of bromine, it is to be noted that the extreme variation in the ratio Ag : AgBr is from 0·574400 to 0·574498 or 1 part in 5745, whilst that in the atomic weight is from 79·901 to 79·933 or 1 part in 2500. The general mean values are given in Table I.

A discussion of all the available data for the ratio of silver to silver bromide, both direct and indirect, has been given by Clarke (" A Recalculation of the Atomic Weights," 4th Edition, *Mem. Nat. Acad. Sci.*, 1920, **16**, 71) and need not be attempted here. The best direct determinations are those of Baxter (*J. Amer. Chem. Soc.*, 1906, **28**, 1322), whose general mean of 18 determinations of the ratio Ag : AgBr is 0·57445, a figure substantially identical with that calculated by Clarke as the general mean of all determinations.

Possible sources of error in the present determinations are :

(1) errors in weighing; (2) loss of silver in transference; (3) impurity in the silver; (4) loss of silver bromide mechanically or in solution; (5) the presence of chlorine or iodine in the ammonium bromide. The error in weighing was undoubtedly too small to have any significant effect and the mode of transference of silver solution to the precipitation flask would appear to eliminate any risk of mechanical loss. The methods used for the preparation of pure silver have been shown to yield a metal containing less than 1 part of impurity in 300,000 parts of silver (Briscoe and Little, J., 1914, **105**, 1320). There can be little doubt that the chief error in the determination of weight lay in the nephelometric estimation of the silver lost (4) in washings and retained by the flask and filter : a careful review of the analytical details leads to the conclusion that this error was not greater than 0·0001 g., but it was probably the one really significant error in the determinations. With regard to the purity of the bromine, it is certain that in such a prolonged fractionation the whole of any chlorine and iodine originally present would have become concentrated in opposite end fractions : therefore the identity of the results obtained with these fractions shows that the chemical purification subsequent to fractionation had so far reduced the proportion of these halogens that their effect on the atomic weight of bromine was inappreciable.

The final mean value of the ratio Ag : AgBr now found differs from Baxter's value by less than 1 part in 100,000, and the rounded mean value of the atomic weight Br = 79·92, with a probable error ± 0·0031, confirms the accepted atomic weight.

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NEWCASTLE UPON TYNE.   [*Received, November 3rd*, 1924.]

XXIV.—*The Use of Fused Borax in the Determination of the Atomic Weight of Boron.*

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THOUGH a few determinations of the atomic weight of boron have been made by ascertaining the ratio of boron halides to silver, the majority have depended in one way or another upon weighing anhydrous borax in the form of borax-glass. A detailed discussion of the results may be found in Clarke's " A Recalculation of the Atomic Weights " (*Mem. Nat. Acad. Sci.*, 1920, **16**, 205) and it is sufficient here to give a list of the determinations. Table I records all the previous data, classified according to the nature of the method employed : the wide divergence among the results renders

the "probable errors" obviously valueless as a measure of the weight to be given to each determination, and they are, therefore, omitted.

TABLE I.

Previous Determinations of the Atomic Weight of Boron.

A. Determinations dependent upon weighing fused borax :

1826. 1849.	Berzelius ⎱ Laurent ⎰	*Estimation of water in borax.*	*11·023*
1869.	Dobrovolsky.	*Estimation of water in borax.* 1st series.	*10·859*
		2nd series.	*11·529*
1892.	Hoskyns-Abrahall.	Decahydrate to borax glass.	10·703
1893.	Ramsay and Aston.	Decahydrate to borax glass.	10·946
		Borax glass to sodium chloride.	10·955
		Borax glass to silver chloride.	11·059
1898.	Armitage.	Decahydrate to borax glass.	10·986
		Borax glass titrated with sulph- uric acid.	10·933
1918.	Smith and van Haagen.	Borax glass to sodium sulphate.	10·904
		Borax glass to sodium fluoride.	10·903
		Borax glass to sodium carbonate.	10·905
		Borax glass to sodium nitrate.	10·899
		Borax glass to sodium chloride.	10·901
		Mean of all determinations.	10·964
		Mean excluding the first four results.	10·939

B. Determinations of the ratio of a boron halide to silver or silver halide :

1892.	Hoskyns-Abrahall.	$BBr_3 : 3Ag$.	10·800
1899.	*Gautier.*	$BBr_3 : 3AgBr$.	*11·016*
		$BCl_3 : 3AgCl$.	*10·947*
1922.	Hönigschmid and Birkenbach.	$BCl_3 : 3AgCl$.	10·840
			10·818
			10·825
		Mean excluding Gautier's results.	10·827

C. Determinations of ratios which do not involve fused borax or a boron halide :

1893.	Rimbach.	$Na_2B_4O_7 10H_2O$: hydrochloric acid solution.	11·006
1899.	*Gautier.*	$B_2S_3 : 3BaSO_4$.	*11·024*
		$B_4C : 6CO_2$.	*10·997*
1923.	Stock and Kuss.	$B_2H_6 : 6H_2$.	10·806

References : Berzelius, *Pogg. Ann.*, 1826, **8**, 1 ; Laurent, *J. pr. Chem.*, 1849, **47**, 415 ; Dobrovolsky, *Doctoral Dissertation, Kiev*, 1869 ; Hoskyns-Abrahall, *J.*, 1892, **61**, 650 ; Ramsay and Aston, *J.*, 1893, **63**, 211 ; Armitage, P., 1898, **14**, 22 ; Smith and van Haagen, *Carnegie Inst. Washington*, Publication No. **267**, 1918 ; Gautier, *Ann. Chim. Phys.*, 1899, [vii], **18**, 352 ; Hönigschmid and Birkenbach, *Ber.*, 1923, **56**, [B], 1467 ; Rimbach, *Ber.*, 1893, **26**, 164 ; Stock and Kuss, *Ber.*, 1923, **56**, [B], 314 ; *Z. anorg. Chem.*, 1923, **128**, 49.

Certain of these determinations (printed in italics) are unsatisfactory. In Group A, those of Berzelius and Laurent have no pretensions to great accuracy, Dobrovolsky's two series are so

gravely discordant as to be valueless; and Abrahall's results are definitely those of preliminary analyses: thus these may be excluded, making the mean result for the Group, B = 10·939. In Group B, Gautier's results show discordance so grave, and so unaccountable in a halide ratio, as to necessitate their immediate exclusion : the remaining results give the mean value B = 10·827. In Group C, Gautier's determinations involve eccentric ratios apparently unsuitable for atomic weight determination. The two remaining values may be retained, but are not pertinent to the point now to be discussed.

Reviewing all the results in Groups A and B not excluded for the reasons given, it is immediately obvious that those dependent upon fused borax have a general tendency to be higher by about 0·1 than those deduced from halide ratios. As experience has shown that the halide ratios usually afford a very trustworthy means of determining atomic weights, and as, moreover, determinations in this laboratory, which will form the subject of another communication, confirmed the general result thereby attained, we were led to suspect that in the use of borax there lay some hitherto unsuspected source of systematic error.

The present determinations were therefore undertaken with a two-fold object : first, to obtain independent confirmation of the values for the atomic weight of boron obtained by earlier workers by the analysis of borax; and secondly, to attempt to ascertain whether the fractional crystallisation of boric acid from aqueous solution produces any change in the isotope ratio of boron. As, for reasons which will appear in due course, the results give no information on the second point and as the general nature of such an enquiry has been discussed elsewhere (Robinson and Briscoe, preceding paper), this secondary object need but be mentioned here in explanation of the nature of the boric acid used as starting material.

Outline of the Method.

Of the possible means of analysing borax, its titration with aqueous hydrochloric acid was chosen because the experimental procedure is relatively simple and therefore little liable to error, and because borax can thus be referred directly to silver chloride, for which the antecedent atomic weights are well known. Rimbach (*loc. cit.*), in his work upon the titration of borax decahydrate, has shown that the reaction proceeds quantitatively according to the equation :

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3.$$
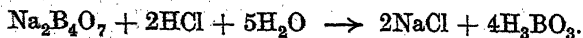
Preliminary tests described later showed that the end-point could

be observed with an accuracy sufficient for our purpose, and the work of Smith and van Haagen afforded the strongest evidence that fused borax was a definite compound well suited to precise work. Therefore the following method was adopted :

Borax, prepared from boric acid and pure sodium carbonate, was purified by fractional crystallisation with centrifugal drainage of the crystals, and the borax decahydrate obtained was fused in platinum vessels in an electrically heated muffle furnace in a current of dry air free from carbon dioxide. The resultant borax glass was weighed, dissolved in water, and titrated with $N/5$-hydrochloric acid solution delivered from a weight burette; the titration being completed by the addition of $N/100$-acid solution from an accurately calibrated burette, using methyl-red as indicator. The acid was standardised by taking a weighed quantity and precipitating the whole of the chlorine as silver chloride, which was collected, dried, and weighed. Hence the ratio actually determined was $Na_2B_4O_7 : 2AgCl$.

The Determination of Weight.

All weighings of borax and silver chloride were made on the special Oertling balance sensitive to 0·01 mg. or less, already described (Robinson and Briscoe, *loc. cit.*), with weights carefully calibrated for relative weight in air and all usual precautions. Fused borax was weighed directly on the balance pan : silver chloride was weighed in the tared bottle used to collect the precipitate.

The standard acid solution was weighed in a stoppered burette, using another similar burette as tare, on a standard No. 7 S.W. Oertling balance carrying a load of 300 g. in each pan and sensitive to 0·1 mg. A second set of calibrated weights was used in this case. As the standard solution only served as a means of referring borax to silver chloride, the relation of the second set of weights to the first is immaterial.

The relative vacuum weights of borax and silver are given to the nearest 0·01 mg., those of standard acid to the nearest 0·5 mg. The vacuum corrections applied were calculated using the densities : silver chloride, $D = 5·50$; borax, $D = 2·357$ (Smith and van Haagen, *loc. cit.*).

Preparation of Reagents.

The *water* and *nitric acid* were prepared by the methods described in a recent communication (Robinson and Briscoe, *loc. cit.*) and the *silver* used was a part of the stock prepared for the work there described.

Hydrochloric Acid.—About 3 litres of pure reagent acid, main-

tained at boiling point in a glass flask, were treated for 30 minutes
with a rapid current of chlorine gas from a cylinder of liquid
chlorine, and the excess of chlorine was then boiled off. Thus any
traces of bromine and iodine were removed. The acid then stood
over-night with copper foil, previously cleaned with nitric acid and
distilled water, to remove arsenic.
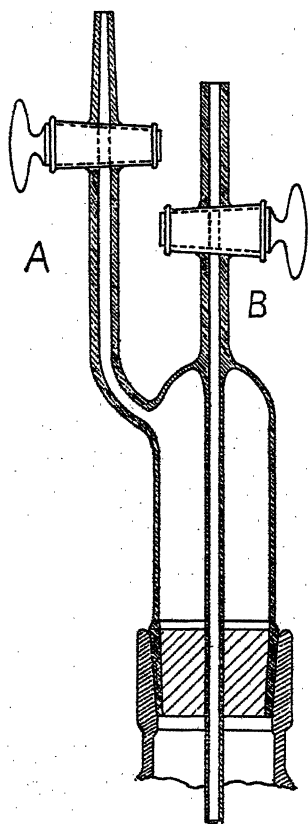
FIG. 1.   FIG. 2.
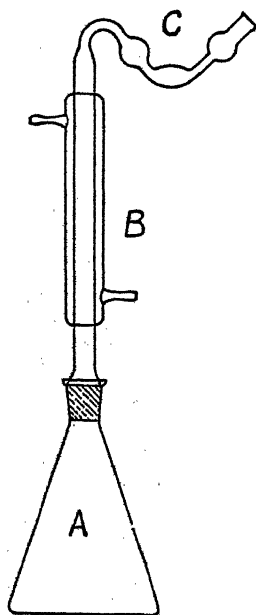
Next day the acid was transferred to a resistance glass still
fitted with a ground-in condenser, heated for 15 minutes to cause
a vigorous evolution of hydrogen chloride gas and thus to eliminate
any remaining volatile impurity, and finally diluted to a density
of 1·10 and twice distilled, considerable head and tail fractions
being rejected in each distillation. The main fraction from the
second distillation was used forthwith for the preparation of the
standard acid. The approximate strength of the acid having been
determined by diluting a weighed portion and titrating it against

fused borax, the requisite volume of the acid was transferred to the storage bottle and diluted to 4000 c.c. with pure water.

In order to ensure, as far as possible, that the concentration of the standard acid should remain constant during the series of titrations, the storage bottle was fitted with a well-ground glass stopper of the form shown in Fig. 1, where A is a stopcock and capillary tube for delivery of acid and B is a second tube, passing to the bottom of the bottle and also fitted with a stopcock to admit air when, the bottle being inverted, acid was withdrawn. Before each withdrawal of acid the contents of the bottle were mixed by vigorous shaking and, in order to minimise the volume of acid withheld from this agitation, the tube B was made of capillary bore. This stopper was wired in place and was not removed during the whole series of standardisations and analyses. Before use, the bottle had been well cleaned and rinsed, allowed to stand for some weeks full of approximately $N/5$-hydrochloric acid, and then again well washed with water.

A quantity of approximately $N/100$-acid was prepared by diluting in a calibrated flask a weighed quantity of the standard $N/5$-acid : thus it was possible by use of an appropriate factor to convert the volume of $N/100$-acid used in each titration to the corresponding *weight* of $N/5$-acid, which was added to the weight determined in the weight burette.

In the standardisation of the $N/5$-acid, a weighed quantity was delivered into a slight excess of aqueous silver nitrate, prepared from pure silver and nitric acid, and the precipitated silver chloride was collected, washed, and weighed by the method already described (Robinson and Briscoe, *loc. cit.*). In this case, of course, the chloride found nephelometrically in the washings and ammoniacal rinsings was calculated to silver chloride and added to the observed weight.

The essential data of the standardisations are given in Table II.

<div align="center">TABLE II.</div>

	I.	II.
Vacuum weight of acid taken	154·4826 g.	160·9230 g.
Vacuum weight of silver chloride	4·52544 g.	4·71377 g.
Ratio, silver chloride : hydrochloric acid ...	0·0029294	0·0029292
Mean value of ratio ..:...........................	0·0029293	

All flasks and burettes used here and in the titrations were carefully calibrated by weighing out with water in the usual way.

<div align="center">*Fractional Crystallisation of Boric Acid.*</div>

About 14 kilos of commercial boric acid supplied by Messrs. Borax Consolidated Ltd, but of unknown origin, were fractionally

crystallised (about 70 crystallisations) until two series, A and B, each of 19 fractions, were obtained. Each fraction contained about 350 g. of boric acid dissolved in 1500 c.c. of water. The fractions were contained in 2-litre round Jena flasks, fitted with loose glass stoppers to exclude dust : crystallisation was effected by slowly heating the whole set of flasks to boiling on a large hot plate and allowing them to cool over-night. The liquor was removed from each flask by pouring off through a filter of copper gauze which retained all fine crystals : then the filter was reversed and liquor from the flask next in the series was poured in through the filter, thus rinsing the fine crystals back into the flask from which they had come. In this way, beginning with the head (most soluble) fraction, all the liquors were moved up one place at each crystallisation, and distilled water was added to the tail fraction. After several (usually three or four) crystallisations, the tail fraction disappeared and the head liquors were evaporated to form a new head fraction. Both series were systematically recrystallised after this fashion and by careful management the fractions were kept reasonably constant in size and number.

After the 60th crystallisation of both series, about 1150 crystallisations in all having been made in each, the extreme head and tail fractions were rejected and the heads A30 and B30, the tails A14 and B15 and the middle fractions A23 and B24 were taken for conversion into borax.

Preparation and Purification of Borax.

In order to obtain strictly comparable samples of borax the operations here described were carried out simultaneously on all six samples of boric acid.

About 120 g. of boric acid were added gradually to a slight excess (about 0·5%) over the calculated equivalent of pure sodium carbonate dissolved in about 200 c.c. of hot water. The sodium carbonate, originally very pure, had been twice recrystallised from water and was spectroscopically free from potassium. The solution was boiled to remove carbon dioxide, filtered whilst hot, and allowed to cool slowly without movement until about one-tenth of the borax had crystallised out. Then the clear liquor was poured off quickly into another vessel and further cooled with agitation, yielding a main crop of fine crystals of borax decahydrate, which were filtered with suction and immediately transferred to glass tubes for centrifugal drainage. The drainage tubes had in the bottom a thick pad of dry cotton wool covered with a wad of small filter papers and a porcelain disk, they were filled with the damp salt, closed by corks covered with filter paper, and centrifuged for

10 minutes at a speed of 2500 revolutions per minute. Thus the mother-liquor was very effectively removed.

The salt, contained in a platinum dish, was first dehydrated in an electrically-heated silica muffle, kept at 200—300° until intumescence ceased, and then fused by raising the temperature to about 700—800°. It thus formed a perfectly clear glass having only a faint blue tinge due to copper derived from the wire gauze filter mentioned above. Some difficulty was experienced at first in dissolving the borax glass in water : later, it was found that if the dish containing the fused glass were floated on cold water the mass developed numerous cracks which allowed water to penetrate the glass and greatly hastened solution. To dissolve the glass, the dish containing it was wholly immersed in water in a covered Durosil beaker heated over a Rose burner : solution was usually complete in about 2 hours.

After fusion, the borax was recrystallised four times from water in the manner already described, with centrifugal drainage of the main crop at each stage. Thus each sample was recrystallised five times in all, about one-tenth of the material in the head fraction and the same amount in the tail fraction being rejected each time. The crystallisations were done in covered Erlenmeyer flasks of Durosil, both these and the beakers having been thoroughly cleaned and boiled out with water for several days before use.

Tests for the chief impurities, carried out on the mother-liquors (head fraction) from each crystallisation, in which the impurities present tended to concentrate, gave a valuable indication of the purity of the main fraction without sacrifice of material therefrom.

Copper was estimated colorimetrically in an ammoniacal solution containing 1 g. of borax decahydrate; the standard solution of copper sulphate contained 1 part of copper in 100,000 parts, and in each case a " blank " test was made on the reagents alone. The head fractions from the earlier crystallisations contained traces of copper, but those from the final crystallisation of all six samples were absolutely free from copper.

Phosphate.—Mother-liquor equivalent to 1 g. of borax decahydrate was treated hot with nitric acid, ammonium nitrate, and ammonium molybdate. No trace of yellow ammonium phosphomolybdate was observed at any stage of the purification.

Sulphate.—The solution of borax was acidified with hydrochloric acid, treated with barium chloride solution, boiled, and kept, covered, over-night. The mother-liquor from the third recrystallisations showed traces of sulphate, but tests on the crystals gave negative results. Two further recrystallisations were made on each

sample and the mother-liquors from these gave negative results on the sulphate tests.

Chloride.—Nitric acid and silver nitrate were added to a solution containing 1 g. of crystallised borax. The third recrystallisation showed a slight opalescence; later tests were negative.

The final main fractions of borax were partly dehydrated by standing for 3 weeks over solid potassium hydroxide in desiccators and were then stored in stoppered bottles, capped to exclude dust.

Fusion of the pure borax was carried out in a platinum dish in the electrically heated muffle in a current of air, free from carbon dioxide and dried over solid caustic potash. The weight of borax taken was such as to yield from 3—10 g. of resultant "glass," as required, and the dehydration and fusion were conducted in the manner described above. When a clear glass was obtained, usually after about 1—1½ hours' fusion, a further period, in no case less than 2 hours, was allowed for complete dehydration. A shallow dish was used for fusion, and thus a large surface of borax was exposed. Samples of the molten glass were taken in two ways: (i) by pouring small beads on to a clean cold platinum surface; (ii) by dipping the bottom of a clean platinum crucible into the melt. In the latter case the glass adhered whilst hot, but, on cooling, cracked off in pieces weighing about 0·3 g. The samples were immediately transferred to, and kept in, a desiccator containing solid caustic potash.

As tests showed that when a bead of the glass weighing about 2 g. was kept on the balance pan for 3 days its weight did not change appreciably, this method of storage was evidently satisfactory. In every case the glass was weighed within 2 days after its fusion.

Method of Analysis.

Preliminary tests with a number of indicators showed that under the conditions of the titration methyl-red gave much the sharpest colour change, especially when the end-point chosen was slightly on the acid side. Under these conditions in $N/10$-borax solution, 2—3 drops of $N/100$-acid or alkali gave a considerable and sharp colour change.

During further tests which showed that the end-point in the borax titration was unaffected by moderate additions of boric acid and sodium chloride, it was observed that in a solution made from boric acid and salt, in the concentration which would be produced in the titration, the end-point was quite indefinite. This curious fact had no direct significance in the analyses now reported, but its further investigation at a future time is proposed.

The titrations were made by two distinct methods described below.

(a) *Using the weight burette.* Weighed beads of borax glass were dissolved to a 2% solution in water by boiling in a covered flask. After cooling, a quantity of $N/5$-acid, calculated to be 99% of that required for complete neutralisation, was added from the weight burette, a fixed volume of a stock solution of methyl-red was pipetted in, and the titration was completed by adding $N/100$-acid from a burette. The quantity of the latter required to give a match with a standard of definite pink shade could be ascertained with certainty within 0·1 c.c. Afterwards a measured excess of $N/100$-acid was added, then a measured excess of an equivalent solution of borax sufficient to make the solution distinctly yellow, and the end-point was again determined with $N/100$-acid.

(b) *By direct weighing of the acid solution.* As several of the earlier determinations showed unaccountable discrepancies, which might have been due to loss of borax (by spurting during solution) or of acid (by splashing when pouring in from the weight burette), a method of titration was devised to eliminate the possibility of such errors. The apparatus shown in Fig. 2 consisted of a 200 c.c. conical flask, A, and a reflux condenser, B, with a spray-trap, C, connected to A by a carefully ground joint.

TABLE III.

Data of Titrations of Borax Glass.

Sample number.		Vacuum wt. (g.) of borax glass.	Vacuum wt. (g.) of $N/5$-acid.	Calculated vacuum wt. (g.) of silver chloride.	Ratio : borax glass / silver chloride.	Atomic weight.
A14	1	1·99413	96·6881	2·83229	0·704068	10·961
	2	1·97982	95·9636	2·81107	0·704294	10·977
	3	1·93077	93·5412	2·74011	0·704632	11·001
	3a	0·81470	39·4923	·1·15685	0·704239	10·973
	4	1·01079	48·9751	1·43463	0·704564	10·996
	5	1·04641	50·6956	1·48503	0·704638	11·002
	6	1·03879	50·3263	1·47421	0·704640	11·002
A24	1	1·00759	48·8258	1·43026	0·704481	10·990
	2	1·01246	49·1306	1·43919	0·703494	10·920
	3	2·14923	104·1576	3·05110	0·704412	10·985
	4	1·84391	89·3821	2·61828	0·704245	10·974
	5	1·90780	92·4578	2·70838	0·704407	10·985
	6	1·95549	94·7315	2·77498	0·704686	11·005
A30	1	1·21340	58·8361	1·72349	0·704036	10·958
	2	1·46470	70·9812	2·07926	0·704434	10·987
	3	1·41400	68·5272	2·00737	0·704403	10·985
	4	1·31097	63·5162	1·86059	0·704600	10·999
	5	0·67774	32·8309	0·96172	0·704717	11·007
	6	0·90300	43·6981	1·28005	0·705439	11·059
	7	1·01566	49·1406	1·43948	0·705574	11·069
	8	1·12262	54·2960	1·59050	0·705829	11·087
	9	1·22427	59·2639	1·73602	0·705215	11·043
	10	1·46529	70·9201	2·07747	0·705324	11·051

This apparatus was made in duplicate of Durosil glass and was cleaned with all the precautions already described. In using it, the required amount of $N/5$-acid was weighed in A against another similar flask as tare, the weighed borax was carefully slid down the dry side of the flask into the acid, the condenser was fitted, a little pure water was introduced into the spray trap, and the flask was heated gently over a Rose burner until the borax had completely dissolved (about 1 hour). After cooling, the contents of the bulbs and condenser were rinsed into the flask, these were removed, and the titration was completed with $N/100$-acid as described above. Working in this manner, the total volume of the solution titrated was little greater than that of the $N/5$-acid used.

Statement and Discussion of Results.

Table III gives the essential data of all the analyses made, and the values of the atomic weight of boron calculated therefrom. The results are evidently subject to errors (1) in the weight of borax taken, (2) in the volume of $N/100$-acid used, (3) in the weight of $N/5$-acid used in the titration, and (4) in the standardisation of the $N/5$-acid : the probable magnitude and effect of these errors are shown in Table IV.

TABLE IV.

Probable maximum value of error.	Corresponding variation in the atomic weight of boron.
(1) 0·1 C.c. of $N/100$-acid on 1 g. of borax-glass......	$\pm 0·005$
(2) 0·02 Mg. on 1 g. of borax	$\pm 0·001$
(3) 0·5 Mg. on 50 g. of $N/5$-acid	$\pm 0·001$
(4) Difference between standardisations : 1 in 15,000	$\pm 0·004$
Total maximum error	$\pm 0·011$

Making all due allowance for these errors, it would appear that the value obtained in each titration for the atomic weight of boron should not be in error by more than one or two units in the second decimal place, and there remain among the data considerable differences which must be otherwise explained.

After much worry had been caused by unaccountable and erratic variations in the atomic weight, it became apparent, as data accumulated, that the result was in many cases a function of the duration of fusion of the borax. Fortunately, precise records of the fusions were available : and their correlation with the results is shown in Table V. It is clear that a high atomic weight is always associated with a long period of fusion. The additional results on A30, Nos. 7, 8, 9, and 10, confirm this in a striking way.

The most probable inference is clear : a higher atomic weight corresponds with a lesser amount of acid used to neutralise a given weight of borax, hence to a lesser content of soda (Na_2O) in that

TABLE V.

Notes on Treatment of Samples.

Sample No.		Atomic weight.	Method of analysis.	Condition of fusion of borax glass.
A14	1	10·961		Molten 4—5 hours.
	2	10·977		Extra 5 g. of crystals added
	3	11·001		to residue (1). Fused 3½
			Simultaneous determinations by weight burette method.	hours. Both samples taken together.
	3A	10·973		Extra crystals added to residue (2); fused 3 hours.
	4	10·996		Further amount of crystals
	5	11·002	,,	dehydrated. Fused 6¾
	6	11·002		hours.
A24	1	10·990	Simultaneous determinations by weight burette method.	30 G. of crystals dehydrated
	2	10·920		to fusion; kept molten 2 hours.
	3	10·985		
	4	10·974	,,	Residue further fused 2 hours.
	5	10·985	,,	Residue from 3 and 4 further
	6	11·005		fused 2½ hours.
A30	1	10·958		
	2	10·987		20 G. of crystals dehydrated
	3	10·985	Weight burette used.	and fused 6 hours before
	4	10·999		sampling.
	5	11·007		
	6	11·059	Done in reflux-apparatus in $N/5$-acid.	Residue from (1—5) fused for 4 hours.
	7	11·069		20 G. of crystals dehydrated
	8	11·087	,,	and fused 10 hours.
	9	11·043	Done by weight	Residue from 7 and 8 fused for
	10	11·051	burette method.	a further 7 hours.

borax : therefore, on fusion, borax loses soda and the extent of this loss increases with the duration of fusion.

Molten borax glass is known to volatilise, but previous workers have differed as to whether any decomposition takes place. Waldebott (*J. Amer. Chem. Soc.*, 1894, **16**, 410), as a result of experiments on the fusion of borax, was of the opinion that sodium tetraborate volatilised unchanged; he analysed the fused residue by treatment with ammonium fluoride and found no change in composition. The application of this method to an atomic weight determination was rejected, however, by Smith and van Haagen (*loc. cit.*). On the other hand, Leonard (*Chem. News*, 1898, **77**, 104), in criticism of the determinations of the atomic weight of boron by Armitage (*loc. cit.*), stated definitely that the residue obtained after fusion of borax required less standard acid for neutralisation than the original sample : this corresponds with a loss of soda. Smith and van Haagen assumed that acidic gases from burners had affected Leonard's borax, but no such explanation can be advanced in this case, since an electrically heated furnace was used to fuse the borax. Their own samples of borax glass were fused to constant weight

in a long-necked platinum flask and they concluded that the material condensed in the cooler part of the apparatus was identical in composition with the fused residue, and was pure sodium tetraborate. But their borax had been fused previously in an open crucible, one may infer for about the same time in the case of all samples, and the sample for analysis was taken from the upper portion of the main mass of glass which, by rotation, had been spread in a thin layer over the upper sides of the crucible and cooled quickly. Therefore the volatilisation of this sample in the flask without material change is quite consistent with its having already changed in composition during the open fusion in the way now observed.

Whatever the explanation may be, it seems clear that the borax ratios are subject to grave uncertainty, and the authors are definitely of opinion that all values for the atomic weight of boron determined by methods involving the weighing of fused borax should be entirely rejected in favour of those deduced from analyses of boron halides.

In summarising the present results it seems proper to discard A24, No. 2 for unaccountable discordance and A30, Nos. 6, 7, 8, 9, and 10, because in these cases the fusion was deliberately prolonged. The mean atomic weight deduced from the remaining determinations, $B = 10.99$, is in general agreement with the results previously obtained with fused borax, and is close to the results of Ramsay and Aston for the ratio $Na_2B_4O_7/2AgCl$, but differs widely from the results of determinations of the halide ratios.

For reasons which have been made clear, the authors attach no weight to this result.

XXV.—The Sulphur Compounds of Kimmeridge Shale Oil. Part I.

By Frederick Challenger, James Richard Ashworth Jinks, and John Haslam.

The oil obtained on distillation of the Kimmeridge shale of Dorset is characterised by a very high percentage of sulphur, which is stated to be 5—8% of the crude oil.* This has prevented its use

* References to other shale oils rich in sulphur are given by Demesse and Reaubourg, *Bull. Soc. chim.*, 1914, [iv], **15**, 625.

as a fuel, and although many attempts have been made to remove the sulphur compounds, these have been unsuccessful, excepting perhaps the recent hypochlorite process of Dunstan. The mode of combination of the sulphur has remained unknown (Perkin, *J. Inst. Pet. Tech.*, 1917, **3**, 227; Manfield, *loc. cit.*, 1916, **2**, 164; Craig and others, *loc. cit.*, 1918, **4**, 149).

Through the kindness of Mr. W. Hardy Manfield, who supplied us with several gallons of the crude oil, we have commenced an investigation with the object of identifying some of the sulphur compounds. The question of removing them on a commercial scale has not been considered. The only communication which contains any real information as to the ingredients of this shale oil was made by Williams (J., 1855, **7**, 97), who only examined the bases, which are sulphur-free. The peculiar odour of the oil seems to be due to these pyridine bases and to unsaturated hydrocarbons. In a typical experiment, 3 litres of the crude oil were distilled with steam until practically no more came over. The pale yellow oil (900 c.c.) was separated,* shaken with 200 c.c. of dilute hydrochloric acid (1 to 3), again separated, and the process repeated with 100 c.c. of the acid. The mixture was shaken for an hour and left over-night. The separated oil was shaken for an hour with 150 c.c. of 10% sodium hydroxide, dried over sodium sulphate, and fractionated three or four times at 15 mm. The table shows the fractions obtained and some analytical results :

Fraction.	B. p. at 15 mm.	Sulphur before NaHSO$_3$.	After NaHSO$_3$. S.	C.	H.	Total.
1	35—50°	10·67 10·83				
2	50—70	10·18 10·14	10·04 10·04 10·04	78·84 79·03 78·77	11·25 11·08 11·09	100·13 100·15 99·90
3	70—90	7·12 7·23				
4	90—110	6·38 6·46 6·39				
5	110—130	5·90				
6	130—145	7·04				

The first two fractions (95 c.c.; 140 c.c.) formed pale yellow oils of pleasant odour which on analysis showed the presence of traces of oxygen. They were therefore separately shaken with saturated sodium bisulphite solution, separated, washed, and analysed. The bisulphite extracts with sodium carbonate yielded 1 c.c. of ketones, b. p. 130—150°, which readily combined with semicarbazide.

* The water (9 litres) was extracted with ether, bases and phenols were removed as before, and the residue was added to the main bulk.

After four rectifications of fraction 1 at the ordinary pressure (no hydrogen sulphide was evolved), fractions were obtained of which the first (b. p. 60—110°) contained 14·07, and the last (b. p. above 150°), 7·82% of sulphur. On standing for some weeks, resin was deposited, doubtless arising from olefines or diolefines. On redistillation, water was formed and a sharp odour observed, probably due to unsaturated aldehydes arising from decomposition of some oxidation product.

Removal of Sulphur from Fraction, b. p. 60—110°.—Five c.c. were slowly added to 25 c.c. of sulphuric acid at − 15°. A dark-red colour developed, as with all fractions of the oil. The mixture was well shaken, and after 1½ hours the oil was separated, washed with water, and found to be free from sulphur. It gave no indophenin reaction nor any colour with sulphuric acid, was stable to cold aqueous permanganate, and had a strong odour of toluene. After nitration with sulphuric and nitric acids at 100°, the product slowly solidified to white needles containing nitrogen (m. p. and mixed m. p. with 2 : 4-dinitrotoluene, 71°).

Oxidation of the Fraction, b. p. 50—70°/15 mm.—(a) *With potassium permanganate.* The oil was sealed in a bulb which was added to 200 c.c. of 2% aqueous potassium permanganate, and broken by shaking. After 10 hours' shaking and addition of more permanganate till decoloration ceased, the solution was filtered, acidified with hydrochloric acid, and precipitated with barium chloride, excess of permanganate being removed with alcohol : (1) 0·4462 gave 0·2450 $BaSO_4$; S = 7·54. (2) 0·5106 gave 0·2830 $BaSO_4$; S = 7·61. (3) 0·7808 gave 0·4264 $BaSO_4$; S = 7·50. In (3) the solution was evaporated with nitric acid to remove any oxalates.

(b) *With nitric acid.* About 0·5 g. was shaken for 4 hours with 12 c.c. of water and 5 c.c. of fuming nitric acid and evaporated with hydrochloric acid and salt : 0·5080 gave 0·2695 $BaSO_4$; S = 7·28. 0·5110 gave 0·2766 $BaSO_4$; S = 7·43. About 75% of the total sulphur is obtained as sulphuric acid. This would indicate that alkyl sulphides and mercaptans are not, at any rate, the chief sulphur compounds present, whilst the cyclic polymethylene sulphides also form stable sulphones on oxidation (Trochimovski, *J. Russ. Phys. Chem. Soc.,* 1916, **48,** 1, 880).

Identification of 2-Methylthiophen in a Fraction, b. p. 80—110°.—The fraction (11 g.), mercuric acetate (80 g.), and 230 c.c. of water were shaken for 15 hours. The precipitate (36 g.), which contained much mercurous acetate due to the presence of olefines, was extracted three times with hot alcohol. The insoluble residue decomposed about 225°. 16 G. were distilled with 60 c.c. of hydro-

chloric acid (1 : 2), giving about 3 c.c. of a colourless oil. This had a pure aromatic odour and gave a strong indophenin reaction. With excess of bromine water, long needles, m. p. 86—87°, were obtained. Tribromo-2-methylthiophen melts at 87°, but when mixed with the corresponding 3-methyl derivative, non-separable mixed crystals, m. p. 74°, are obtained (Meyer, *Ber.*, 1885, **18**, 544). 3-Methylthiophen would therefore seem to be absent.

2-*Methylthiophenmercurichloride*, $CH_3 \cdot C_4H_2S \cdot HgCl$.—One c.c. of the regenerated oil was shaken with 10 c.c. of alcohol, 100 c.c. of saturated mercuric chloride solution, and 30 c.c. of 33% sodium acetate solution. The precipitate (2·6 g.) was free from mercurous chloride.* Recrystallised from hot alcohol and then from acetone, it had m. p. 194—195° with slight previous sintering; but when placed in the bath at 190°, its m. p. was 202°. Repeated experiments gave no depression of the m. p. on admixture with authentic 2-methylthiophenmercurichloride. The compound was converted to mercury 2 : 2′-dimethyldithienyl, $(CH_3 \cdot C_4H_2S)_2Hg$, by the method of Steinkopf (*Annalen*, 1921, **424**, 40); m. p. and mixed m. p. 160°. This was converted by mercuric bromide into 2-methylthiophenmercuribromide (Steinkopf, *loc. cit.*); m. p. and mixed m. p. 178°. All these mercury derivatives of thiophen homologues were shown by Steinkopf to sinter slightly before melting. The non-depression of m. p. was, however, very definite. The m. p. of 2-methylthiophenmercurichloride was strongly depressed on admixture with the corresponding thiophen compound.

Identification of Thiophen.—Another specimen of the oil purified as before gave fractions, b. p. 77—83° and 83—93°. With mercuric chloride and sodium acetate these gave mercurous chloride (due to olefines) and traces of a solid which, on repeated crystallisation from alcohol and acetone, gave a strong indophenin reaction and was identified as thiophenmercurichloride by its m. p. and mixed m. p. (180—181°). It strongly depressed the m. p. of 2-methylthiophenmercurichloride.

The presence of thiophen derivatives in the oil explains its behaviour on oxidation. In some cases, Meyer (" Die Thiophen Gruppe," pp. 55, 204) obtained very bad yields of carboxylic acids on oxidation of the alkylthiophens, owing to almost complete decomposition. We find that cold 2% aqueous potassium permanganate completely oxidises thiophen to sulphuric acid, although Angeli and Alessandri (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 314) state that it is stable to alcoholic permanganate.

Our results are in general agreement with those of other workers. Scheibler (*Ber.*, 1915, **48**, 1815; 1916, **49**, 2595; 1919, **52**, 1903)

* Due to previous removal of olefines with mercuric acetate.

examined shale oils rich in sulphur. His method of purification was very complicated, but from a fraction of b. p. 170—180°/360 mm. he obtained with acetyl chloride and aluminium chloride a ketone, possibly propylacetothienone, $C_4H_2PrS\cdot COMe$, and analysed the semicarbazone. Pfaff and Kreutzer (*Z. angew. Chem.*, 1923, **36**, 437) identified 2-methylthiophen in a fraction of lignite tar. by conversion into 2-methylacetothienone.

XXVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part V. The Synthesis of Cyanidin Chloride and of Delphinidin Chloride.*

By DAVID DOIG PRATT and ROBERT ROBINSON.

IN Part II (J., 1923, **123**, 750), it was shown that ω-methoxyacetoveratrone (I) can be obtained by the methylation of ω-hydroxyacetoveratrone by means of silver oxide and methyl iodide. The oily product yielded isomeric semicarbazones, $C_{12}H_{17}O_4N_3$, (*a*) m. p. 205°, and (*b*) m. p. 168°, whilst condensation with β-resorcylaldehyde in presence of hydrogen chloride gave rise to a pyrylium salt characterised as the ferrichloride, $C_{18}H_{17}O_5Cl_4Fe$, m. p. 156°. The unsatisfactory character of the process is emphasised in the memoir quoted and as a preliminary to an attempt to synthesise cyanidin chloride it was clearly essential to work out an entirely novel method of preparation of ω-methoxyacetoveratrone. We desired to proceed from veratric acid in order that the process might subsequently be applied to the trimethyl ether of gallic acid and so lead to a synthesis of delphinidin salts. After unsuccessful trials in other directions, *e.g.*, in attempting the decomposition of diazoacetophenones by methyl alcohol, the solution of the problem was found in an application of the synthesis of acetophenone from benzoyl chloride by way of ethyl benzoylacetate. The action of sodium on ethyl methoxyacetate leads to the sodio-derivative of ethyl αγ-dimethoxyacetoacetate, $MeO\cdot CH_2\cdot CO\cdot CH(OMe)\cdot CO_2Et$, which readily yields *C*-aroyl derivatives. Ethyl αγ-dimethoxy-α-benzoylacetoacetate was decomposed by boiling dilute sulphuric acid with formation of phenylglyoxal in poor yield, but when it was subjected to the prolonged action of cold dilute potassium hydroxide and the mixture was subsequently boiled, ω-methoxyacetophenone (Part II, p. 748) was obtained in accordance with the scheme :—

$$\begin{array}{c} \text{CO·CH}_2\text{·OMe} \\ \text{Ph·CO·C(OMe)·CO}_2\text{Et} \end{array} \xrightarrow{+3\text{KOH}} \begin{array}{c} \text{Ph·CO·CH}_2\text{·OMe} + \text{MeO·CH}_2\text{·CO}_2\text{K} \\ + \text{K}_2\text{CO}_3 + \text{EtOH}. \end{array}$$
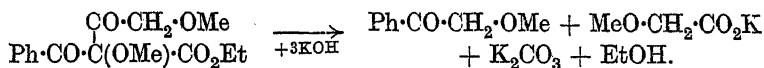
In a similar manner, ω : 4-dimethoxyacetophenone (Part II, p. 750) was derived from anisic acid, and the product of the inter-action of ethyl sodio-$\alpha\gamma$-dimethoxyacetoacetate and veratroyl chloride in dry ethereal solution yielded ω-methoxyacetoveratrone on careful hydrolysis with alkali. The analogous preparation of ω : 3 : 4 : 5-tetramethoxyacetophenone (II) offered no difficulty.

Pure ω-methoxyacetoveratrone is a crystalline substance which gives a single semicarbazone, m. p. 178°, and this is identical with the previously described veratrylmethoxyacetaldehydesemicarb-azone-b, the melting point of which was slowly raised to 178° by repeated crystallisation. Veratrylmethoxyacetaldehydesemicarb-azone-a, m. p. 205°, was the more sparingly soluble of the isomerides and its melting point is not raised on recrystallisation. This sub-stance is plainly the semicarbazone of α : 3 : 4-trimethoxyphenyl-acetaldehyde (III), and the formation of the latter in the methyl-ation of veratroylcarbinol is noteworthy.

MeO	CO·CH₂·OMe	MeO	CO·CH₂·OMe	MeO	CH(OMe)·CHO
MeO		MeO		MeO	
		MeO			
(I.)		(II.)		(III.)	
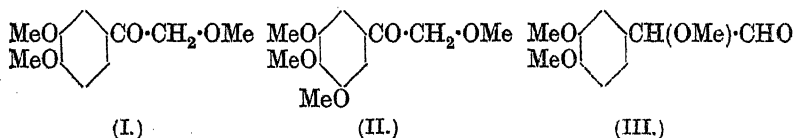
ω-Methoxyacetoveratrone and ω : 3 : 4 : 5-tetramethoxyaceto-phenone are much more soluble in cold than in hot water, a pro-perty which doubtless indicates the formation and decomposition of hydrates. The former ketone on condensation with β-resorcyl-aldehyde in presence of hydrogen chloride yields trimethylfisetinidin chloride (IV), and the derived ferrichloride, m. p. 156°, is identical with the substance obtained as mentioned above. 2-Hydroxy-4 : 6-dimethoxybenzaldehyde and ω-methoxyacetoveratrone con-dense under the agency of hydrogen chloride in ethereal solution with formation of cyanidin chloride pentamethyl ether (V), and this salt is demethylated by means of boiling hydriodic acid in presence of phenol with formation of cyanidin iodide. Cyanidin chloride (VI) was prepared from the iodide in the usual manner and the product exhibited in every detail the properties of cyanidin chloride of natural origin as described by Willstätter and Everest (*Annalen*, 1913, **401**, 189) and Willstätter and Nolan (*ibid.*, 1915, **408**, 13). A direct comparison of the synthetical material with an authentic specimen disclosed no differences existing between them. The production of cyanidin chloride by the reduction of quercetin in acid solution (Willstätter and Mallison, *Sitzungsber. Preuss.*

Akad. Wiss., 1914, 769) constitutes in one sense a synthesis of the substance, and furthermore Willstätter and Kindler, in 1919, made a communication to the Münchner Chemische Gesellschaft concerning experiments which they had conducted on the application of the Willstätter-Zechmeister pelargonidin synthesis to the case of cyanidin ("Wissenschaftliche Forschungsberichte, III, Organische Chemie," R. Pummerer, 2nd Edition, 1923, 150). The details of the results obtained are not yet available.*
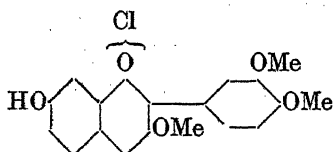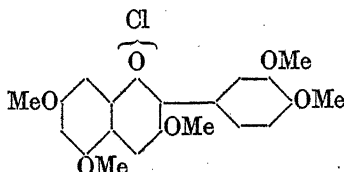
(IV.)   (V.)
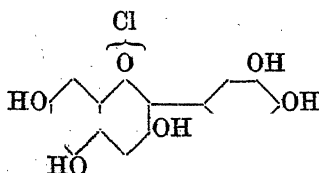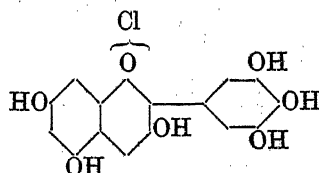
(VI.)   (VII.)

The synthesis of delphinidin chloride (VII) followed the lines of that of cyanidin chloride, delphinidin chloride hexamethyl ether being obtained from hydroxydimethoxybenzaldehyde and ω : 3 : 4 : 5-tetramethoxyacetophenone (II). As shown in the experimental portion on page 174, there can be no doubt as to the identity of the synthetical product, obtained on demethylation, with that of natural origin.

E X P E R I M E N T A L.

Ethyl αγ-Dimethoxyacetoacetate.—Ethyl chloroacetate (122 g.) was gradually added with cooling and shaking to a solution of sodium methoxide (from 23 g. of sodium) in anhydrous methyl alcohol (200 c.c.). The mixture was refluxed until neutral, most of the alcohol then removed, and the residue mixed with brine and ether. The dried ethereal solution on fractionation yielded 85 g. of ethyl methoxyacetate, b. p. 131°.† Sodium (8 g.), cut in thin slices,

* Willstätter, Zechmeister, and Kindler have now published their work (*Ber.*, 1924, **57**, [*B*], 1938).

† This substance can also be obtained by the hydrolysis of methoxyacetonitrile by Pinner's method. Ethyl ethoxyacetate (Henry, *Ber.*, 1871, **4**, 706); ethyl αγ-diethoxyacetoacetate (Conrad, *Ber.*, 1878, **11**, 58; Erlenbach, *Annalen*, 1892, **269**, 28). In order to avoid the possibility of replace-

was added in one portion to ethyl methoxyacetate (100 g.); the reaction, which soon commenced, was controlled by cooling in melting ice when necessary. The thick syrup which resulted was treated with 50% acetic acid (45 c.c.) and saturated brine and extracted with ether. The ethereal layer was separated, washed with aqueous sodium carbonate, dried with anhydrous sodium sulphate, and distilled; 40 g. of a colourless oil, b. p. 130°/15 mm., were obtained (Found : C = 50·4; H = 7·4. $C_8H_{14}O_5$ requires C = 50·5; H = 7·4%). This ester is moderately readily soluble in water, and its alcoholic solution gives a violet coloration with ferric chloride, the shade being bluer than that developed by ethyl acetoacetate under similar conditions.

ω : 4-*Dimethoxyacetophenone.*—In the first place, experiments on the hydrolysis of the condensation product from ethyl sodio-αγ-dimethoxyacetoacetate and benzoyl chloride were made. After boiling with dilute sulphuric acid and distillation in a current of steam, a yellow distillate was obtained, and this by suitable treatment yielded phenylglyoxaldiphenylhydrazone, m. p. 152°. When, however, the product was boiled with dilute aqueous sodium hydroxide, ω-methoxyacetophenone was obtained in small yield and identified as the semicarbazone, m. p. 85°. ω : 4-Dimethoxy-acetophenone may be obtained in the following manner : Sodium (2·7 g.) was granulated under toluene, washed with ether, suspended in anhydrous ether (150 c.c.), and ethyl αγ-dimethoxyacetoacetate (22·3 g.) gradually added. A sodio-derivative separated from the solution and, when the sodium had disappeared, anisoyl chloride (20 g.) was added in one portion. A gentle reaction occurred and after 1 hour the process was completed by heating on the steam-bath under reflux during 4 hours. Next day water was added, the ethereal layer dried over sodium sulphate, and after removal of the solvent 35 g. of a pale yellow oil remained. The whole was agitated for 12 hours with 2·5% aqueous potassium hydroxide (500 c.c.), and the liquid then boiled for 3 hours, cooled, nearly saturated with potassium carbonate, and extracted with ether; 7·5 g. of the ketone, m. p. 40°, were obtained.

On condensation with 6-aminopiperonal in alcoholic solution by means of potassium hydroxide, ω : 4-dimethoxyacetophenone yields

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ment of the ethyl group of the esters by methyl and the production of mixtures Mr. N. L. Matthews has employed methyl chloroacetate and condensed this with sodium methoxide in dry methyl-alcoholic solution in the cold. Methyl chloroacetate (108 g.) yielded methyl methoxyacetate (70 g.), b. p. 129°/754 mm. Methyl methoxyacetate (100 g.) reacted with sodium (9 g.) to give a product from which *methyl* αγ-*dimethoxyacetoacetate*, b. p. 129°/17 mm., could be isolated (Found : C = 47·5; H = 7·1. $C_7H_{12}O$ requires C = 47·7; H = 6·8%). The yield was 40—50% of that required by theory.

3-*methoxy*-6 : 7-*methylenedioxy*-2-(4-*methoxyphenyl*)*quinoline*,   which crystallises from methyl alcohol in colourless laminæ, m. p. 152°.

ω-*Methoxyacetoveratrone*   (I).—Ethyl   αγ-dimethoxyacetoacetate (36·2 g.) was gradually added to finely granulated sodium (4·4 g.) suspended in anhydrous ether (225 c.c.).   Formation of the sodio-derivative appeared to be complete after an hour, and a solution of distilled veratroyl chloride (38 g.) in ether (150 c.c.) was intro-duced, causing a mild reaction.   The mixture was gently heated on the steam-bath for 2 hours, allowed to remain over-night, and heated during a further 2 hours.   After washing with water, drying, and evaporating the ether, there remained 63 g. of a pale orange, viscous liquid which could not be crystallised.   The whole product was hydrolysed by vigorous agitation for 9 hours with cold 2·5% aqueous potassium hydroxide (800 c.c.) and finally by boiling the clear solution for 5 hours.   The ketone was isolated by extraction with ether after the addition of much potassium carbonate and purified by distillation; 22 g. of an oil, b. p. 190°/15 mm., were obtained which solidified.   The substance crystallises from light petroleum containing a little benzene in colourless prisms, m. p. 62° (Found : C = 63·1; H = 6·8. $C_{11}H_{14}O_4$ requires C = 62·9; H = 6·7%).   When a little of this substance is melted under water and the mixture cooled, a clear solution is obtained from which the ketone may be precipitated as an oil either by heating or by the addition of an alkali carbonate or hydroxide.   The substance is very readily soluble in organic solvents with the exception of light petroleum.   On condensation with 6-aminopiperonal, it yields 3 - *methoxy* - 6 : 7 - *methylenedioxy* -2 -(3 : 4-*dimethoxyphenyl*)*quinoline*, which crystallises from ethyl alcohol in slender needles, m. p. 155°, and exhibits a violet fluorescence in alcoholic solution.

Fisetinidin Chloride Trimethyl Ether (IV).

A slow stream of hydrogen chloride was passed through an ice-cold solution of β-resorcylaldehyde (2 g.) and ω-methoxyaceto-veratrone (3 g.) in dry ether (40 c.c.), when the liquid became yellow and then red and crystallisation commenced after 20 minutes. The passage of the gas was discontinued after 30 minutes and after several hours the pyrylium salt, which exhibited an intense green lustre, was collected, washed with ether, and dried (3·4 g.).   The ethereal mother-liquors were washed with dilute hydrochloric acid and a ferrichloride (0·2 g.) was precipitated.   This derivative crystallises from acetic acid in reddish-brown needles, m. p. 156°, and its properties are identical with those of the ferrichloride previously prepared from the product of methylation of veratroyl-carbinol (*loc. cit.*).   Fisetinidin chloride trimethyl ether dissolves in

hot 7% hydrochloric acid to an orange-red solution and separates completely on cooling in reddish-brown, prismatic needles exhibiting a green reflex (Found in material dried in a vacuum : C = 56·1 ; H = 5·3. $C_{18}H_{17}O_5Cl,2H_2O$ requires C = 56·2 ; H = 5·5%). This salt darkens at 135° and decomposes at 188—189°. It is reddish-violet by transmitted light and makes a violet smear on paper. Its alcoholic solutions are intensely reddish-violet and the orange solution in concentrated sulphuric acid exhibits a green fluorescence. Sparingly soluble in cold water, it dissolves on warming to an orange-red solution which on dilution is rapidly decolorised with formation of the ψ-base. The violet colour-base is precipitated when sodium acetate is added to a moderately concentrated aqueous solution of the salt, but if a dilute solution is treated with sodium acetate the appearance of the violet colour is transient and the ψ-base is obtained. isoAmyl alcohol extracts the salt completely from an acid aqueous solution and the addition of sodium acetate to the red alcoholic extract gives a violet solution the colour of which fades. The oxonium salt is regenerated from solutions of the colour-base and ψ-base by the addition of hydrochloric acid.

Cyanidin Chloride Pentamethyl Ether (V).

In order to obtain good results in this preparation, it is very necessary that the materials employed should be pure. Hydrogen chloride was passed for 1 hour through a solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (4·5 g.) and ω-methoxyacetoveratrone (5·2 g.) in ether (50 c.c.). The solution quickly became crimson and crystallisation of the product was induced by scratching after 30 minutes from the commencement. The tube containing the mixture and a dish containing solid potassium hydroxide were together covered by a bell-jar and after several hours the salt was collected, washed with ether, and dried (5·5 g.). The salt crystallises from alcohol containing a little hydrogen chloride in small, red needles, m. p. 152°, which in mass exhibit an old-gold sheen, but give a chocolate-brown smear on paper (Found, in material dried in a vacuum over phosphoric oxide and potassium hydroxide : C = 51·7 ; H = 5·9 ; Cl = 14·9. $C_{20}H_{21}O_6Cl,HCl,2H_2O$ requires C = 51·6 ; H = 5·6 ; Cl = 15·2%). The same dichloride crystallised from a mixture of alcohol and concentrated aqueous hydrochloric acid in slender needles, m. p. 152° (Found : C = 51·5 ; H = 5·5 ; Cl = 15·4%). From 7% aqueous hydrochloric acid, the salt separates in long, orange-brown needles which form a crystalline crust exhibiting a green reflex (Found, in material dried in a vacuum : C = 53·2 ; H = 6·0. $C_{20}H_{21}O_6Cl,3H_2O$ requires C = 53·7 ; H = 6·0%). The substance is readily soluble in the simple

alcohols to reddish-violet solutions the colour of which fades on
dilution with water and can then be restored by the addition of a
mineral acid. The *ferrichloride* crystallises from acetic acid, in
which it is very sparingly soluble, in reddish-brown, prismatic
needles, m. p. 194—200° (decomp.), exhibiting a bronze lustre. The
chloride is insoluble in chloroform, but this derivative is moderately
readily soluble and when the hot saturated solution is rapidly
concentrated to one-quarter of its bulk the ferrichloride separates
in microscopic needles exhibiting an intense green lustre.

Cyanidin Chloride (VI).

The foregoing pentamethyl ether (3·2 g.) and phenol (15 g.)
were added to hydriodic acid (180 c.c.; *d* 1·7) and the mixture was
boiled for 30 minutes in an atmosphere of carbon dioxide. Water
(2 vols.) and much ether were added to the cooled solution and, on
standing, glistening needles with a bright green reflex separated.
The substance (1·8 g.) had properties identical with those of cyanidin
iodide prepared by the demethylation of paeonidin chloride of
natural origin (Willstätter and Nolan, *Annalen*, 1915, 408, 136).
The iodide (3 g.) was thoroughly ground with aqueous sodium
acetate, the bluish-violet colour-base separated, thoroughly washed,
and heated to boiling with 3% aqueous hydrochloric acid (100 c.c.)
in presence of a trace of silver, and filtered, 50 c.c. more 3%
hydrochloric acid being used for washing. Concentrated hydro-
chloric acid (50 c.c.) was added and, on standing, the dark red
solution deposited the salt completely in masses of short, reddish-
brown prisms that had a green lustre (Found : C = 52·5; H = 4·1.
$C_{15}H_{11}O_6Cl,H_2O$ requires C = 52·8; H = 3·8%). This product
showed all the characteristic reactions of cyanidin chloride, and a
direct comparison with a specimen of the substance of natural
origin disclosed no difference in properties of any kind. The
behaviour on heating, appearance of the crystals under the micro-
scope, formation of colour-base and ψ-base, solubilities in aqueous
and alcoholic acid solutions, colour of acid solutions, absorption
spectrum of the solution in ethyl alcohol, and the reactions with
ferric chloride, sodium carbonate, sodium acetate, potassium acetate
in alcoholic solution, lead acetate and Fehling's solution were all
examined. Willstätter and Everest (*loc. cit.*) state that cyanidin
on oxidation with hydrogen peroxide yields a yellow, crystalline
product closely resembling a flavonol colouring matter. There is,
however, no clear evidence that quercetin can be obtained by the
oxidation of cyanidin and furthermore it is remarkable that no
chromone or chromonol derivative has yet been prepared by
oxidising a benzopyrylium salt. We have made numerous experi-

ments with the object of achieving this transformation, but any definite products isolated have been either carboxylic acids or coumarin derivatives. This investigation proceeds.

ω : 3 : 4 : 5-*Tetramethoxyacetophenone* (II).—Sodium (2·5 g.), granulated under toluene and washed with ether, was suspended in ether (120 c.c.), and ethyl αγ-dimethoxyacetoacetate (20 g.) slowly added. When the formation of the sodio-derivative appeared to be complete, an ethereal solution of trimethylgalloyl chloride (24·5 g.) was added in one portion, and the mixture heated gently on the steam-bath for 8 hours. The product was isolated (34 g.) and shaken for 12 hours with 2·5% aqueous potassium hydroxide. The solution was boiled for 4 hours, and the ketone isolated as in the case of ω-methoxyacetoveratrone. The yield was 9 g. of a colourless oil, b. p. 212°/15 mm., which solidified in contact with light petroleum. The substance crystallises from benzene–light petroleum in colourless needles, m. p. 54°, and closely resembles ω-methoxyacetoveratrone (Found : C = 60·0; H = 6·3. $C_{12}H_{16}O_5$ requires C = 60·0; H = 6·6%). The *semicarbazone* crystallises from aqueous alcohol in long, colourless needles, m. p. 158°.

3-*Methoxy*-6 : 7-*methylenedioxy*-2-(3 : 4 : 5-*trimethoxyphenyl*)*quinoline* crystallises from ethyl alcohol in colourless needles, m. p. 159°, and exhibits a violet fluorescence in alcoholic solution. Its salts, e.g., the sparingly soluble *hydrochloride*, are yellow. The *methosulphate* is orange-yellow and it is evident from a comparison of this substance with the intensely coloured delphinidin chloride hexamethyl ether that the quinolinium and benzopyrylium nuclei function quite differently as chromophores. It may well be that the methoxyl groups are able to decentralise the cationic valency of the pyrylium nucleus and so produce changes of orbits of electrons owing to recurrent redistribution of the charge, whilst, on the other hand, the powerfully basic quinolinium nucleus is able to ignore the claims of the weak auxochromes. We are thus led to anticipate that the aminophenylquinolinium salts will resemble tinctorially the related hydroxyphenylbenzopyrylium salts and it is hoped that an experimental test of this point will be made.

Delphinidin Chloride Hexamethyl Ether (corresponding with VII).

Hydrogen chloride was passed through an ice-cold solution of ω : 3 : 4 : 5-tetramethoxyacetophenone (4 g.) and 2-hydroxy-4 : 6-dimethoxybenzaldehyde (3 g.) in dry ether (50 c.c.), crystallisation of the product in crimson needles and prisms having a dark green reflex occurring after about 1 hour. Next day, the salt (4 g.) was collected and a further quantity (0·7 g.) was obtained from the ethereal mother-liquor. The substance crystallises from alcohol

containing a trace of hydrogen chloride in long, red needles, m. p. 163—164° (Found, in material dried in a vacuum : C = 58·5; H = 5·8. $C_{21}H_{23}O_7Cl,0·5H_2O$ requires C = 58·4; H = 5·6%). The substance exhibits a green lustre and is reddish-violet by transmitted light. It is readily soluble in the simple alcohols and moderately soluble in chloroform to a reddish-violet solution. The dark red colour of the solution in water rapidly fades and an almost colourless ψ-base is precipitated. Faintly acid solutions are also decolorised on great dilution, but addition of acid restores the colour of the pyrylium salt. The *ferrichloride* crystallises from glacial acetic acid in brownish-red needles which have a dark green appearance in mass. This derivative, m. p. 169—170°, is readily soluble in acetone, chloroform, or the simple alcohols. The *sulphate* crystallises from dilute sulphuric acid in slender, red needles with green reflex, m. p. 225° (decomp.).

Delphinidin Chloride (VII).

Delphinidin chloride hexamethyl ether (3·0 g.) was demethylated by means of a boiling mixture of hydriodic acid (180 c.c.; d 1·7) and phenol (15 g.) during 30 minutes, a slow current of carbon dioxide being passed through the containing vessel. The cooled liquid deposited clusters of long, pointed, brown needles together with some squat prisms, and these were collected, washed with ether, and dried (2·0 g.). The iodide was converted into chloride by treatment at 60° with silver chloride in alcoholic solution in a silver-mirrored vessel. The filtered solution was mixed with an equal volume of concentrated hydrochloric acid, and the amorphous precipitate so obtained allowed to remain, when it slowly became resolved into a mass of microscopic needles. The substance was isolated and crystallised by solution in 5% hydrochloric acid and addition of 30% acid to the filtered solution so as to make the concentration of hydrochloric acid about 25%. The brown, crystalline mass was dried in a vacuum (Found : C = 49·4; H = 4·0. $C_{15}H_{11}O_7Cl,1·5H_2O$ requires C = 49·4; H = 3·8; H_2O = 7·4%). According to Willstätter and Weil (*Annalen*, 1916, 412, 178), delphinidin chloride crystallises from hydrochloric acid of 20% or greater concentrations with $1·5H_2O$, which is completely lost in a vacuum. Our product did not behave in this way, but the circumstance was an accident, since when the material was powdered and again exposed to a vacuum it lost 7·6%. The anhydrous salt does not melt below 350°. The hydrates containing $1H_2O$, $2H_2O$, and $4H_2O$ have been prepared by the methods devised by Willstätter and Weil in order to observe the crystalline forms, which were found to agree with the descriptions of these authors.

The absorption spectrum of an alcoholic solution of the chloride, the formation of the ψ-base, the behaviour of aqueous and acid solutions on shaking with ether, ethyl acetate and *iso*amyl alcohol, the reactions with ferric chloride in aqueous and alcoholic solutions and with sodium carbonate, sodium bisulphite, lead acetate, and Fehling's solution were all examined with results identical with those described in the case of delphinidin chloride of natural origin by Willstätter and Mieg (*Annalen*, 1915, **408**, 61) and Willstätter and Weil (*loc. cit.*). We were not able to make a direct comparison, but the properties of delphinidin chloride are so characteristic and have been recorded in such detail that we can entertain no doubt as to the identity of the synthetical product with that obtained by the hydrolysis of the pigments of the wild purple larkspur and the blue-black pansy.

XXVII.—*Synthesis of certain Higher Aliphatic Compounds. Part I. A Synthesis of Lactarinic Acid and of Oleic Acid.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

THIS investigation originated in a desire to develop methods which could be applied to the synthesis of the naturally occurring, unsaturated fatty acids and attention was concentrated in the first place on attempts to synthesise oleic acid. An examination of the literature shows that this acid has been obtained from 10-ketostearic acid,* $CH_3 \cdot [CH_2]_7 \cdot CO \cdot [CH_2]_8 \cdot CO_2H$, by reduction to hydroxystearic acid followed by conversion to iodostearic acid and treatment with alcoholic potassium hydroxide (see p. 179). It therefore became an object to devise a process for the preparation of acids of the form $R \cdot [CH_2]_m \cdot CO \cdot [CH_2]_n \cdot CO_2H$, which should be applicable to a case such that $R \cdot [CH_2]_m I$ cannot be readily converted into an organo-zinc or magnesium derivative. After numerous trials in other directions, it was found that ethyl sodio-*n*-heptylmalonate and 9-carbethoxy-nonoyl chloride condensed in ethereal solution to a product which

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* The carboxyl group of stearic acid is numbered 1 in this communication in order to avoid confusion with the Geneva nomenclature. This system has been frequently adopted in recent literature.

gave a very small yield of 10-ketostearic acid on prolonged hydrolysis
with boiling 1% aqueous oxalic acid. A considerable improvement
was effected by starting with ethyl acetoacetate instead of ethyl
malonate. Ethyl sodio-2-acetylnonoate and 9-carbethoxynonoyl
chloride were brought into reaction in ether, and the resulting ester,
$CH_3 \cdot [CH_2]_6 \cdot CAc(CO_2Et) \cdot CO \cdot [CH_2]_8 \cdot CO_2Et$, was cautiously hydro-
lysed at first by cold dilute alkali, then by boiling dilute sulphuric
acid and finally by boiling dilute aqueous sodium hydroxide. The
sparingly soluble, crystalline sodium salt of 10-ketostearic acid
separated on cooling the solution. This acid melts at 83° and the
product of the action of sulphuric acid and water on stearolic acid,
after a wasteful process of purification, melts at the same temper-
ature, alone or mixed with the synthetic specimen. It is probable
that the isomeride accompanying 10-ketostearic acid in the crude
material derived from stearolic acid is 9-ketostearic acid and we are
engaged in the preparation of this substance in order to determine
the proportions in which the acetylenic bond is hydrated in the two
possible directions. The synthesis of oleic acid by way of 10-keto-
stearic acid and 10-iodostearic acid affords a proof that the double
bond is in the position $\Delta^{9:10}$ or $\Delta^{10:11}$ and in order to eliminate the
latter alternative we are engaged in an attempt to synthesise stearolic
acid. We have found that this acid may be reduced to oleic acid by
means of zinc dust and hydrochloric acid in presence of titanous
chloride in acetic acid solution. Elaidic and stearic acids are not
produced under the conditions described (p. 177) and the reaction
indicates that oleic acid has the *cis*-configuration. The addition of
hydrogen iodide to stearolic acid has been previously shown to
lead to isomeric iodoelaidic acids which can be transformed into
elaidic acid (Arnaud and Posternak, *Compt. rend.*, 1910, **150**, 1130,
1525).

In the course of investigations on the constituents of certain fungi,
Bougault and Charaux found that several species of *Lactarius*
contained a ketostearic acid, termed lactarinic acid, in the free state
(*Compt. rend.*, 1911, **153**, 572, 880). The results obtained by
applying the Beckmann transformation to the oxime of lactarinic
acid showed that the substance must be 6-ketostearic acid and we
have now confirmed this conclusion by synthesis. Ethyl sodio-
2-acetyl-*n*-tridecoate and 5-carbethoxyvaleryl chloride react in
ethereal solution so as to produce the ester

$$CH_3 \cdot [CH_2]_{10} \cdot CAc(CO_2Et) \cdot CO \cdot [CH_2]_4 \cdot CO_2Et,$$
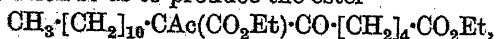
which by graduated hydrolysis yields lactarinic acid,

$$CH_3 \cdot [CH_2]_{11} \cdot CO \cdot [CH_2]_4 \cdot CO_2H.$$
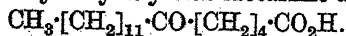
We are greatly indebted to Professor Bougault for a specimen of the
acid of natural origin, and a careful comparison proved the identity

of this with the synthetical product.   At the suggestion of Professor
H. S. Raper, we have also synthesised 4-ketopalmitic acid in order
to render possible a direct comparison with a substance prepared
by the oxidation of palmitic acid.   In this case, ethyl sodio-2-acetyl-
n-tridecoate and 3-carbomethoxypropionyl chloride gave the ester
$CH_3\cdot[CH_2]_{10}\cdot CAc(CO_2Et)\cdot CO\cdot[CH_2]_2\cdot CO_2Me$, and by hydrolysis the
desired keto-acid, $CH_3\cdot[CH_2]_{11}\cdot CO\cdot[CH_2]_2\cdot CO_2H$.

<div align="center">EXPERIMENTAL.</div>

Reduction of Stearolic Acid to Oleic Acid.—Hydrochloric acid
(50 c.c. of 40%) was slowly added to a gently boiling mixture of
acetic acid (30 g.), aqueous titanous chloride (10 g. of 15%), stearolic
acid (3 g.), and zinc dust (10 g.) contained in a flask closed by a tube
bearing a Bunsen valve.   After 2 hours, zinc dust (5 g.) and acetic
acid (20 c.c.) were added and the process was completed by boiling
for 2 hours.   The product was mixed with ether, the separated
ethereal solution well washed with water, and the acid contained
converted into its barium salt (3·5 g.), which was twice crystallised
from a mixture of benzene (8 vols.), ethyl alcohol (1 vol.), and a
trace of water.   The free oleic acid obtained from the barium salt
and hot dilute hydrochloric acid was dried in light petroleum
(b. p. 40—45°) with anhydrous sodium sulphate, and the solvent
removed.   The residue, consisting of the pure acid, crystallised
on cooling as a glassy mass which froze at 12·5° in one experiment
and at 13° in another.   These freezing points were taken with the
thermometer immersed in the liquid, and the specimen freezing
at 13° froze at the same temperature when mixed with a specimen
of pure oleic acid prepared from olive oil, for which we are indebted
to Professor A. Lapworth.   The characteristic dimorphism exhibited
by oleic acid has been described by Kirchner (*Z. physikal. Chem.*,
1913, 79, 789), and when the acid freezing at 13° was maintained
at about 12°, the nuclei of the new modification gradually formed
and closely resembled in appearance under the lens the photographs
reproduced in the memoir quoted above.   The transformed
material melted just above 16°.   When the acid, dissolved in 300
times its weight of water and one-third of its weight of potassium
hydroxide, was oxidised at 0° by the gradual addition of 0·5N-
potassium permanganate, dihydroxystearic acid was produced in
almost theoretical amount; it was best isolated by filtration after
the passage of sulphur dioxide.   The substance, crystallised from
alcohol–benzene, melted at 132°, alone or mixed with a specimen
prepared from oleic acid from olive oil.   The melting point 136°
given in the literature for this acid is too high.

9-Carbethoxynonanilide.—Ethyl hydrogen sebacate (22 g.) (Grün

and Wirth, *Ber.*, 1922, **55**, 2207) was heated on the steam-bath for 3 hours with thionyl chloride * (66 g.), the thionyl chloride removed completely by distillation under reduced pressure and exposure of the residue to a vacuum, and 9-carbethoxynonoyl chloride, thus obtained in good yield, treated with an excess of aniline. The *anilide* crystallised from light petroleum containing a little benzene in colourless needles, m. p. 63° (Found : C = 70·9 ; H = 8·7. $C_{18}H_{27}O_3N$ requires C = 70·8 ; H = 8·8%).

10-*Ketostearic Acid.*—The condensation of ethyl sodio-*n*-heptyl-malonate with 9-carbethoxynonoyl chloride was carried out like that in the case of the related derivative of acetoacetic acid.   The product was an oil which on hydrolysis by alkali gave heptylmalonic and sebacic acids, but no ketostearic acid.   Dilute sulphuric acid gave a similar result, but 1% aqueous oxalic acid caused partial hydrolysis in the desired direction and a very small yield of 10-keto-stearic acid, m. p. 77°, could be isolated after boiling during a week. The process was obviously unsatisfactory and was abandoned in favour of the following method.

Sodium (1·2 g.) was granulated under toluene, washed with ether, suspended in ether (75 c.c.), and a solution of ethyl 2-acetylnonoate (11·5 g.) (Jourdan, *Annalen*, 1879, **200**, 105) in ether (75 c.c.) gradually added.   The clear solution of the sodio-derivative obtained by gentle heating was cooled in melting ice and treated with 9-carbethoxynonoyl chloride (12·5 g.) in ether (20 c.c.).   After 1 hour, the mixture was boiled for 10 minutes, cooled, washed with water, and the ether evaporated.   The residue was shaken with 5% aqueous sodium hydroxide (200 c.c.) for 2 days and then, after acidification with acetic acid, collected again by means of ether, boiled during 24 hours with 5% sulphuric acid (300 c.c.), and the mixture steam-distilled; the oil in the distillate was methyl *n*-octyl ketone (Jourdan, *loc. cit.*).   The residue in the flask was once more collected by means of ether and boiled during 1·5 hours with 5% aqueous sodium hydroxide (100 c.c.).   On cooling, the gelatinous precipitate first formed rapidly changed to colourless leaflets, m. p. 212°.   The acid obtained from this salt crystallised from alcohol and from light petroleum in colourless plates, m. p. 83°, and at the same temperature when mixed with 10-ketostearic acid derived from stearolic acid as described below.   The two specimens were carefully compared and no differences could be discerned. Stearolic acid was dissolved in concentrated sulphuric acid (5 parts) as recommended by Baruch (*Ber.*, 1884, **27**, 174), but water was not added after 12 hours, the solution being filtered by glass wool

* Purified by distillation after boiling under reflux with 1% of aluminium chloride and 1% of sulphur.

and kept in an open vessel. The crust which formed at the surface
was removed from time to time, drained on porous porcelain,
crystallised from alcohol, converted into sodium salt, which was
also crystallised from alcohol, finally the recovered acid was
crystallised twice from light petroleum and twice from benzene.
The product melted at 83°, whereas the crude acid melts at about
72° and the highest recorded melting point is 76°.   10-*Hydroxystearic
acid*, prepared in theoretical yield by the reduction of pure sodium
10-ketostearate in dry alcohol by means of sodium, melts at 84·5°.
This acid yields 10-iodostearic acid by the action of phosphorus
tri-iodide and water, and Arnaud and Posternak (*Compt. rend.*,
1910, **150**, 1525) have carefully examined the products of the action
of alcoholic potassium hydroxide on this iodostearic acid, a reaction
first investigated by Saytzeff (*J. pr. Chem.*, 1887, [ii], **35**, 387).   The
former authors showed that oleic acid, hydroxystearic acid, and
isomeric elaidic acids can be isolated.

Ethyl   2-Acetyl-n-tridecoate, $CH_3 \cdot [CH_2]_{10} \cdot CHAc \cdot CO_2Et.$—12·2
Grams of an oil, b. p. 185°/17 mm., were obtained according to the
usual method employing sodium (1·4 g.), alcohol (17·5 g.), ethyl
acetoacetate (11·8 g.), *n*-undecyl iodide (17 g.); the time of reaction
was 3·5 hours (Found : C = 72·1; H = 11·1. $C_{17}H_{32}O_3$ requires
C = 71·8; H = 11·3%).

6-Ketostearic Acid (Lactarinic Acid).—Ethyl hydrogen adipate,
prepared by a method analogous to that employed by Grün and
Wirth (*loc. cit.*) in the semi-hydrolysis of diethyl sebacate, was
converted into the acid chloride by means of pure thionyl chloride.
5-Carbethoxyvaleryl chloride (8·5 g.) dissolved in ether (10 c.c.)
was added to a solution of ethyl sodio-2-acetyl-*n*-tridecoate (13·5 g.)
in ether (75 c.c.) at 0°; after remaining ½ hour at room temperature,
the mixture was boiled under reflux for 15 minutes. The washed
and isolated product was shaken for 16 hours with 5% aqueous
sodium hydroxide (300 c.c.), collected as in the previous example,
and boiled with 5% sulphuric acid (600 c.c.) for 24 hours. Steam
distillation separated some methyl *n*-dodecyl ketone, m. p. 33—34°
(Krafft, *Ber.*, 1882, **15**, 1708), and the residue in the flask was
collected and heated for 4·5 hours with boiling 5% aqueous sodium
hydroxide (200 c.c.). The sodium salt (4·2 g.) which crystallised
on cooling was collected, and the acid isolated and crystallised from
alcohol. The colourless plates melted at 87°, alone or mixed with
an authentic specimen of lactarinic acid (Found : C = 72·7;
H = 11·3. Calc. for $C_{18}H_{34}O_2$, C = 72·5; H = 11·4%).

The *oxime*, m. p. 59—61°, crystallised from light petroleum in
microscopic needles and was transformed by concentrated sulphuric
acid at 100° into an amide crystallising from alcohol in colourless

needles, m. p. 104°. These m. pt's. agree with those given by Bougault and Charaux (*loc. cit.*).

3 - *Carbomethoxypropionanilide*, $CO_2Me \cdot CH_2 \cdot CH_2 \cdot CO \cdot NHPh$.— Methyl hydrogen succinate, being a solid, m. p. 58°, was used in preference to the corresponding ethyl derivative in the synthesis of 4-ketopalmitic acid. Succinic anhydride, conveniently obtained by the action of thionyl chloride on the acid, was converted into the semi-ester by the method of Bone, Sprankling, and Sudborough (J., 1904, **85**, 530). 3-*Carbomethoxypropionyl chloride*, derived from the acid by the action of thionyl chloride, is a colourless liquid, b. p. 93°/18 mm., and reacts with aniline with formation of 3-carbo-methoxypropionanilide, which crystallises from light petroleum-benzene, as also from ether, in colourless needles, m. p. 97—99° (Found : C = 63·8 ; H = 6·4. Calc. for $C_{11}H_{13}O_3N$, C = 63·7 ; H = 6·3%). The same substance has been prepared by the action of methyl alcohol and hydrogen chloride on succinanil (van der Meulen, *Rec. trav. chim.*, 1896, **15**, 341 ; Hoogewerth and van Dorp, *ibid.*, 1898, **17**, 200).

4-*Ketopalmitic Acid.*—A solution of 3-carbomethoxypropionyl chloride (6 g.) in ether (30 c.c.) was added to the sodio-derivative from ethyl 2-acetyl-*n*-tridecoate (11 g.) and granulated sodium (0·9 g.) in ether (320 c.c.). The mixture was cooled in ice-water, kept over-night, and boiled under reflux for ½ hour. The washed and isolated product was hydrolysed by shaking for 6 hours with 5% potassium hydroxide (300 c.c.), boiling for 30 hours with 5% sulphuric acid (250 c.c.) and for 3 hours with 5% potassium hydroxide. The potassium salt did not separate on cooling and, on acidification of the solution, 5·1 g. of almost pure 4-ketopalmitic acid were obtained. The substance crystallises from light petroleum in colourless clusters of waxy, lanceolate plates, m. p. 91—92° (Found : C = 71·3 ; H = 11·0. $C_{16}H_{30}O_3$ requires C = 71·1 ; H = 11·1%). The *oxime* is readily soluble in most organic solvents and crystallises from light petroleum in colourless needles, m. p. 54°.

XXVIII.—*A Synthesis of Myricetin and of a Galangin Monomethyl Ether Occurring in Galanga Root.*

By JAN KALFF and ROBERT ROBINSON.

ALLAN and ROBINSON (J., 1924, **125**, 2192) have described an extremely simple method of preparation of 7-hydroxy-3-methoxy-flavone by hydrolysis of the product of the action of benzoic anhydride and sodium benzoate on ω-methoxyresacetophenone at 180—185°. On applying the reaction to ω-methoxyphloraceto-phenone (Slater and Stephen, J., 1920, **117**, 316), we have now obtained an excellent yield of 5 : 7-dihydroxy-3-methoxyflavone (I), which is identical with the galangin monomethyl ether isolated from galanga root, the rhizome of *Alpinia officinarum* (Hance), by Testoni (*Gazzetta*, 1900, **30**, ii, 327). The formation of phloro-glucinol and benzoic acid by the aërial oxidation of an alkaline solution of the substance was observed by A. G. Perkin and Allison (J., 1902, **81**, 472) and led to the suggestion that it is galangin 3-monomethyl ether. This conclusion is now confirmed by syn-thesis, and the occurrence of the methyl group in this position in the molecule of a naturally occurring flavonol is of interest because there is reason to believe that certain of the anthocyanidins are similarly constituted in respect of this structural detail. The attractive view that the anthocyanin and anthoxanthin pigments are intimately and genetically related derives support from the accumulation of such coincidences. Galangin itself is obtained by demethylation of the methyl ether, and this flavonol has been previously synthesised by v. Kostanecki and Tambor (*Ber.*, 1899, **32**, 2260).
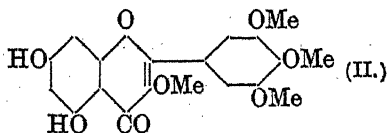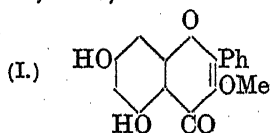
Myricetin was first isolated by A. G. Perkin and Hummel (J., 1896, **69**, 1287) from the bark of *Myrica nagi* (Thunb), and as a result of this and subsequent investigations (Perkin, J., 1902, **81**, 204; 1911, **99**, 1721; Perkin and Phipps, J., 1904, **85**, 62) has been regarded as 3 : 5 : 7 : 3' : 4' : 5' :-hexahydroxyflavone (II with H in place of Me). Myricetin is somewhat widely distributed in nature, and it is the flavonol which should yield a delphinidin salt on reduction in acid solution. The synthesis of the colouring matter is a further example of the new and convenient method of prepara-tion of the flavonols. ω-Methoxyphloroacetophenone was heated

with trimethylgallic anhydride and sodium trimethylgallate, and the product hydrolysed. The 5 : 7-dihydroxy-3 : 3′ : 4′ : 5′-tetra-methoxyflavone (II) thus obtained yields myricetin on demethyl-ation. Phloroglucinol is converted in this manner into myricetin through two isolated intermediate stages only, and the synthesis is also available as a preparative method.

<div align="center">EXPERIMENTAL.</div>

Galangin 3-Monomethyl Ether (I).—A mixture of ω-methoxy-phloroacetophenone (5 g.), sodium benzoate (6 g.), and benzoic anhydride (15 g.) was heated (oil-bath at 180°) during 8 hours, after which alcohol (75 c.c.) was added to the dark red, semi-solid mass, and potassium hydroxide (8·5 g.) in water (10 c.c.) gradually introduced to the boiling solution. After refluxing for $\frac{1}{2}$ hour, the greater part of the alcohol was evaporated, the residue dissolved in water, and the flavonol precipitated as a brown powder by saturating the liquid with carbon dioxide, collected, washed, and dried (6·5 g.). The substance was purified through its *diacetyl* derivative, prepared by the action of boiling acetic anhydride during 2 hours. After two crystallisations from alcohol (charcoal), the substance was obtained in long, very pale yellow needles, m. p. 175—176° (Found : C = 65·3; H = 4·4. $C_{20}H_{16}O_7$ requires C = 65·2; H = 4·4 %). Testoni (*Gazzetta*, 1900, **30**, ii, 327) states that the diacetate derived from the galangin monomethyl ether from galanga root melts at 175—176°. The diacetylgalangin methyl ether was hydrolysed by means of an excess of 10% aqueous potassium hydroxide on the steam-bath. The phenol precipitated by hydrochloric acid may be crystallised from alcohol, acetic acid, or ethyl acetate in rectan-gular, yellow plates, m. p. 299°, soluble in dilute aqueous potassium hydroxide to an intense yellow solution (sodium salt, yellow needles) and in sulphuric acid to a yellow solution exhibiting green fluor-escence (Found : C = 67·2; H = 4·4. $C_{16}H_{12}O_5$ requires C = 67·6; H = 4·3%). The properties of this substance agree with those ascribed to natural galangin monomethyl ether by Testoni (*loc. cit.*) and the identity was proved by the fact that the melting point of the synthetical material was not lowered by admixture with the natural product, for a specimen of which we are greatly indebted to Professor A. G. Perkin. Demethylation by means of boiling hydriodic acid (*d* 1·7), mixed with a quarter of its weight of acetic anhydride, during 40 minutes resulted in the formation of galangin, m. p. 214—215°, after crystallisation from alcohol.

Myricetin 3 : 3′ : 4′ : 5′-Tetramethyl Ether (II).—Pyridine (52 g.) was gradually added to a solution of trimethylgalloyl chloride (35 g.) (Perkin and Weizmann, J., 1906, **89**, 1655) in ether (250 c.c.)

and, after 2 hours, ice and then water was gradually introduced, and the trimethyl gallic anhydride, which is sparingly soluble in ether, collected, washed with dilute aqueous sodium carbonate solution, and dried (yield 75%). This product melted at 159° (corr.) and was employed without further purification (Fischer and Freudenberg, *Ber.*, 1913, **46**, 1129, give 160—161° [corr.] as the m. p. of the pure substance). A mixture of trimethylgallic anhydride (23 g.), sodium trimethylgallate (10 g.), and ω-methoxyphloro-acetophenone (4·5 g.) was heated at 175° for 3 hours. The mixture was at first completely fluid, but as the reaction proceeded it became a dark red paste. As in the previous example, the flavonol was isolated by treatment of the crude product with an alcoholic solution of potassium hydroxide (8 g.) and precipitation of the phenolic material by means of carbon dioxide after removal of the alcohol and solution of the residue in water.

The crude material (8·2 g.) was acetylated by boiling with an excess of acetic anhydride, and the derivative crystallised from alcohol. $3:3':4':5'$-*Tetramethylmyricetin diacetate* was obtained in long, pale yellow needles, m. p. 159° (corr.) (Found : C = 60·3; H = 4·9. $C_{23}H_{22}O_{10}$ requires C = 60·2; H = 4·9%). On hydrolysis by means of boiling concentrated hydrochloric acid, this derivative yields myricetin tetramethyl ether, which crystallises from alcohol in thin, glistening, pale yellow plates, m. p. 276—277·5° (Found : C = 60·6; H = 4·8. $C_{19}H_{18}O_8$ requires C = 60·9; H = 4·8%). This sparingly soluble substance is almost devoid of mordant dyeing properties.

Myricetin.—The tetramethyl ether was demethylated by treatment for 2 hours with a boiling mixture of colourless hydriodic acid (d 1·7) (4 parts) and acetic anhydride (1 part). The red, crystalline myricetin hydriodide was collected, decomposed by hot water, and the yellow precipitate isolated. The substance crystallised from aqueous alcohol in bright yellow needles and showed all the highly characteristic reactions of myricetin as described by Perkin and his collaborators (*loc. cit.*). The remarkable behaviour with alkalis and with mineral acids, the reactions with lead acetate and ferric chloride, and the dyeing properties were examined. The melting point was about 360°, but, as stated by Perkin, the determination is difficult on account of blackening. For this reason, the substance was converted in the usual manner into the hexa-acetate, which crystallised from alcohol in long, silky, colourless needles, m. p. 214—215° * (corr.) (Found : C = 56·8; H = 3·7. Calc. for $C_{27}H_{22}O_{14}$, C = 56·8; H = 3·9%).

* The melting point, 211–212°, given in the literature is presumably uncorrected.

We are greatly indebted to Professor A. G. Perkin for a specimen of myricetin hexa-acetate. The derivative prepared from natural myricetin when mixed with the synthetical material did not depress its melting point. Direct comparison further confirmed the identity of the specimens.

We desire to thank the Ramsay Memorial Fellowship Trust for a Fellowship (Netherlands) which has enabled one of us to take part in this investigation.

XXIX.—*Researches on Residual Affinity and Co-ordination. Part XXIII. Interactions of Trimethylstibine and Platinic and Palladous Chlorides.*

By GILBERT T. MORGAN and VICTOR EMMANUEL YARSLEY.

THE lower chlorides of platinum and palladium combine additively with ammonia, pyridine, thioethers, selenoethers and the trialkylphosphines and -arsines to give rise to co-ordination compounds of the general types $PtCl_2,2X$, $PtCl_2,4X$, $PdCl_2,2X$, and $PdCl_2,4X$.

In the case of the amine and pyridine derivatives of platinous chloride, there is considerable foundation for the belief that the compounds $PtCl_2,2X$ exist in *cis*- and *trans*-modifications, the four associating units and the central platinum atom being regarded as being in the same plane. A change of orientation from this coplanar arrangement to a tetrahedral configuration would, however, result in the disappearance of the above-mentioned *cis*- and *trans*-isomerism.

This change may occur with an increase in the atomic volume of the associating units and although coplanar arrangement may be the rule with amines it by no means follows that this configuration will persist in the additive compounds with phosphines and arsines.

The compounds with trimethyl- and triethyl-phosphines were discovered by Cahours and Gal (*Compt. rend.*, 1870, 70, 897; 71, 208, 1381), who obtained two products of empirical formula $PtCl_2,2PR_3$, in each case, one white and the other yellow. Transformation of the latter to the former modification was noticed on heating, but no evidence was given, or has since been forthcoming, that the two substances have the same molecular complexity. These authors also obtained two isomeric arsenical derivatives, $PtCl_2,2As(C_2H_5)_3$, both of which were yellow but differed in solubility. But here again there is no evidence as to molecular complexity.

In the experiments described below, chloroplatinic acid and palladous chloride have been treated in turn with trimethylstibine. With the platinic compound reduction occurs giving rise to trimethylstibine dichloride, and the resulting platinous compound then interacts with more trimethylstibine forming one or two additive compounds according as to whether the reaction occurs in aqueous or alcoholic solution. In the former medium, an orange product is formed which is insoluble in water and organic solvents. In alcohol, this orange compound is precipitated, but a soluble substance is also formed which crystallises from organic media in pale yellow leaflets.

Analyses and molecular-weight determinations indicate that the soluble yellow product is *bistrimethylstibinedichloroplatinum* (II). The orange substance is evidently either isomeric or polymeric with this yellow compound, for it passes quantitatively into the latter at 60° or when left for several months at the ordinary temperature.

Owing to the insolubility of the orange compound in all neutral solvents, its molecular complexity cannot be determined by physical methods, but its structure has been ascertained by preparing it in two other ways.

$$H_2PtCl_6 + (CH_3)_3Sb = H_2PtCl_4 + (CH_3)_3SbCl_2.$$
$$PtCl_2 + Sb(CH_3)_3.$$

(I.) $[Pt,4(CH_3)_3Sb]PtCl_4.$
orange insoluble dimeride.

$[2(CH_3)_3Sb,PtCl_2]$ (II.)
yellow soluble monomeride.

$[Pt,4(CH_3)_3Sb]PdCl_4.$

↑PdCl₂.

(I .) $[Pt,4(CH_3)_3Sb]Cl_2$
soluble.

K_2PtCl_4.
excess H₂PtCl₄.
excess SbMe₃.
excess H₂PtCl₄.

$H_2PtCl_6.$
(1 mol.)

(IV.) $[Pt,4(CH_3)_3Sb]PtCl_6.$
golden-yellow insoluble.
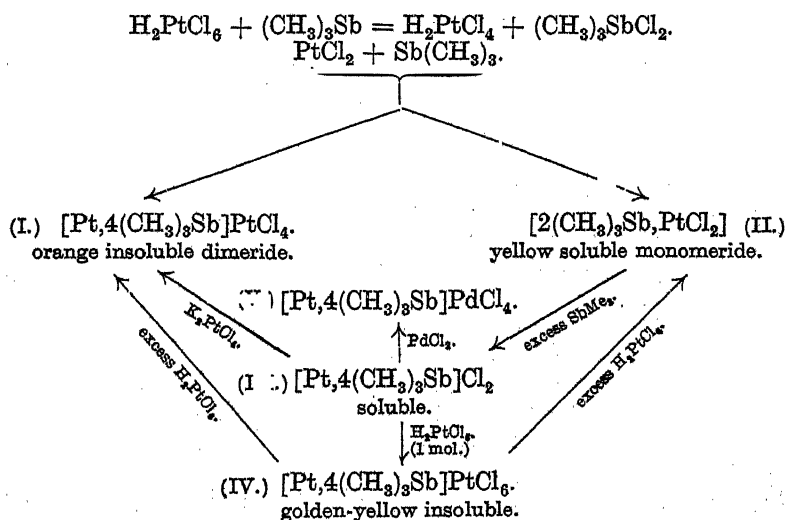
1. With excess of trimethylstibine, the yellow and orange compounds are both converted slowly into the soluble *tetrakistrimethylstibineplatinous chloride* (III), and this salt on treatment with cold aqueous potassium platinochloride gives rise to the orange compound, which is thereby shown to be *tetrakistrimethylstibineplatinous platinochloride* (I). With chloroplatinic acid or palladous

chloride tetrakistrimethylstibineplatinous chloride gives rise respectively to *tetrakistrimethylstibineplatinous platinichloride* (IV) or *tetrakistrimethylstibineplatinous palladochloride* (V).

2. The former of those two salts when hydrolysed with excess of chloroplatinic acid furnishes *bistrimethylstibinedichloroplatinum* (II) and *tetrakistrimethylstibineplatinous platinochloride* (I), in the proportions of 17 : 1.

In the palladium series, trimethylstibine and palladous chloride interact at low temperatures to form an orange additive product, but this changes spontaneously on slight rise of temperature to a yellow substance, *bistrimethylstibinedichloropalladium* (VI). Excess of trimethylstibine converts this to the soluble orange *tetrakistrimethylstibinepalladous chloride* (VII), a soluble salt less stable than

(VI.) $[2(CH_3)_3Sb,PdCl_2]$. $[Pd,4(CH_3)_3Sb]Cl_2$ (VII.)

its platinum analogue, which did not give with palladous chloride an insoluble product corresponding with the orange dimeride of the platinous series.

Digested with dilute hydrochloric acid, the tetrakis compound is converted into a light yellow, crystalline substance, *trimethylstibinedichloropalladium hydrochloride* (VIII), $[(CH_3)_3Sb,PdCl_3]H$, which, unlike the other pallado-derivatives, is stable on keeping.

EXPERIMENTAL.

Trimethylstibine, being spontaneously inflammable in air, was manipulated in the apparatus shown in the accompanying figure. The base was prepared by the Grignard reaction (Hibbert, *Ber.*, 1906, **39**, 160) and converted into trimethylstibine dibromide by running its ethereal solution into bromine diluted with the same solvent.

Weighed quantities of the dibromide are introduced into flask A, together with a small quantity of water and the calculated amount of finely granulated zinc (Kahlbaum No. 1). The air in the apparatus having been previously expelled by a stream of carbon dioxide, the mixture is distilled and the trimethylstibine collected in the graduated receiver B. The reaction vessel E is turned through an angle of 120° by means of the movable rubber joint J, so that the filter disk, L, is raised above the reacting liquids. A slight excess of aqueous platinic or palladous chloride solution is delivered into E from the tap funnel, D, and to this is slowly added the calculated amount of trimethylstibine from the graduated receiver B. As the tertiary stibine is not miscible with aqueous solutions, the chemical combination is facilitated by shaking the vessel E and when the reaction is completed the apparatus is rotated so that the

attachments of vessel E are now in the vertical position as shown by the diagram. By aspiration at K, the liquid contents of E are drawn through the filter, L, on which the insoluble product is collected. The precipitate is now washed with ether introduced through the tap funnel, C, and the ethereal washings are aspirated into the receiver F. Here the aqueous and ethereal filtrates are separated, the former being drawn off into the flask G, whilst the latter is collected in distilling flask, H, which is fitted with a condenser, P.

On distilling off the solvent, a residue is obtained of the ether-soluble product, which is shown below to be trimethylstibine dichloride.

When alcoholic platinic chloride is employed the reaction is more vigorous because of the miscibility of trimethylstibine with this medium. The insoluble product is collected as before on filter L, whilst the alcoholic filtrate and washings are drawn into flask H. On removing the solvent, the residue contains trimethylstibine dichloride and bistrimethylstibinedichloroplatinum (or palladium).

The whole apparatus is so designed that these platinous and palladous derivatives of highly inflammable trimethylstibine can be prepared, collected and desiccated in an inert atmosphere and out of contact with air.

FIG. 1.
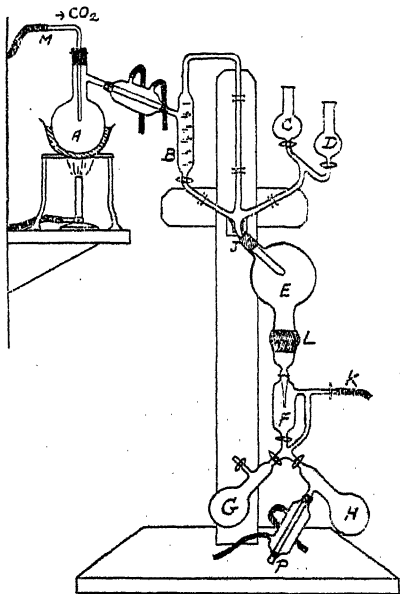
I. *Platinum Series.*

Tetrakistrimethylstibineplatinous Platinochloride (I).—The addition of trimethylstibine to aqueous platinic chloride in the air-free apparatus resulted in the formation of an orange precipitate insoluble in water or in organic media, which was washed successively with water and ether and dried at the ordinary temperature : 0·2200 gave 0·0990 CO_2, 0·0639 H_2O, C = 12·24, H = 3·21; 0·1807 gave 0·0905 AgCl, Cl = 12·39; 0·0819 gave 0·0454 Sb_2S_3, Sb = 39·86; 0·2465 gave 0·0812 Pt, Pt = 32·94. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%.

When left for several months, or rapidly on heating at 65°, this substance undergoes depolymerisation to the pale yellow bistrimethylstibinedichloroplatinum. Both modifications are produced when the interaction of trimethylstibine and platinic chloride is effected in alcoholic solution; the orange dimeric compound is precipitated whereas the monomeric substance remains in solution.

Tetrakistrimethylstibineplatinous platinochloride was also obtained by the following methods, which throw light on its molecular complexity.

1. *From tetrakistrimethylstibineplatinous chloride* (III). A slight excess of aqueous potassium platinochloride was added to tetrakistrimethylstibineplatinous chloride, also dissolved in water, when the orange compound was precipitated quantitatively. This preparation was insoluble in organic solvents and changed at 60° into bistrimethylstibinedichloroplatinum.

2. *From tetrakistrimethylstibineplatinous platinichloride* (p. 189). When treated with a slight excess of aqueous chloroplatinic acid, this platinichloride gave a pale yellow deposit not entirely soluble in organic solvents and leaving in each instance a small amount of orange residue. The ratio of soluble to insoluble product was as 17 : 1. Moreover, when heated at 65°, the orange substance changed in the characteristic manner to the yellow soluble form separating from alcohol in pale yellow leaflets : 0·1139 gave 0·0553 AgCl, Cl = 12·00; 0·1133 gave 0·0653 Sb_2S_3, 0·0364 Pt, Sb = 41·1, Pt = 32·29. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%.

Bistrimethylstibinedichloroplatinum (II).—When trimethylstibine and platinic chloride interact in alcoholic solution, the preceding orange insoluble compound separates forthwith, leaving in solution *bistrimethylstibinedichloroplatinum* and trimethylstibine dichloride. After distilling off the solvent, the latter product is removed by ether, leaving the co-ordination compound in a state of purity : 0·1362 gave 0·0661 AgCl, Cl = 12·32. Molecular weight in chloroform gave $M = 605$. $C_6H_{18}Cl_2Sb_2Pt$ requires Cl = 11·9%; $M = 600$.

This monomeric compound was also prepared by heating its polymeride at 60° for several hours. The preparation crystallised from alcohol in pale yellow leaflets and did not yield the green salt of Magnus when treated with Reiset's chloride, [Pt,4NH_3]Cl_2 : 0·1009 gave 0·0450 CO_2, 0·0303 H_2O, C = 12·12, H = 3·29; 0·1054 gave 0·0526 AgCl, Cl = 12·38; 0·1188 gave 0·0663 Sb_2S_3, Sb = 40·12; 0·1165 gave 0·0379 Pt, Pt = 32·54, M (in chloroform)= 634·7. $C_6H_{18}Cl_2Sb_2Pt$ requires C = 12·17, H = 3·01, Cl = 11·9, Sb = 40·2, Pt = 32·72%; $M = 600$.

The by-product soluble in ether was identified as trimethylstibine dichloride by recrystallisation from this solvent, when it separated in colourless, six-sided crystals : 0·1271 gave 0·1664 AgCl, Cl = 30·02. $C_3H_9Cl_2Sb$ requires Cl = 30·03%. This dichloride is also formed on passing chlorine into an alcoholic solution of bistrimethyl-stibinedichloroplatinum.

When treated in alcoholic solution with hydroxylamine hydro-chloride and sodium acetate, bistrimethylstibinedichloroplatinum was completely reduced. With excess of pyridine, the bistrimethyl-stibine derivative yields well-defined, colourless needles of tetra-pyridineplatinous chloride, readily soluble in water or organic solvents. The pyridine was estimated by the method of Harvey and Sparks (*J. Soc. Chem. Ind.*, 1918, **31**, 41T): 0·0495 gave Py = 55·0; 0·0434 gave 0·0215 AgCl, Cl = 12·25. $C_{20}H_{20}N_4PtCl_2$ requires Py = 54·3, Cl = 12·16%.

Tetrakistrimethylstibineplatinous Chloride (III).—An attempt to prepare this compound by adding excess of trimethylstibine to platinous chloride resulted in the formation of the orange poly-meride. This product, when treated with more trimethylstibine, dissolved and the solution gave immediately a dark orange-brown precipitate readily soluble in water or organic solvents, separating from the latter in orange-brown crystals. These are somewhat plastic and difficult to purify, and hence the compound was charac-terised by conversion into its *chloroplatinate*. For this purpose, the calculated amount of chloroplatinic acid in aqueous solution was mixed with the tetrakis compound, when a golden-yellow deposit was obtained : 0·0802 gave 0·247 Pt, Pt = 30·81. $C_{12}H_{36}Cl_6Sb_4Pt_2$ requires Pt = 30·80%.

Tetrakistrimethylstibineplatinous palladochloride (V), prepared by adding aqueous palladous chloride to an alcoholic solution of the tetrakis compound, crystallised from alcohol in brown leaflets which were very unstable, being decomposed completely on exposure to air for 24 hours : 0·0339 gave 0·0210 Sb_2S_3, 0·0056 Pt, 0·0032 Pd; Sb = 43·9, Pt = 17·08, Pd = 9·46. $C_{12}H_{36}Cl_4SbPtPd$ requires Sb = 43·6, Pt = 17·52, Pd = 9·59%.

Bistri - n - butylstibinedichloroplatinum, $[2(C_4H_9)_3Sb \cdot PtCl_2]$.— Attempts to prepare the higher homologues of trimethylstibine-dichloroplatinum by adding triethylstibine and tri-*n*-butylstibine to aqueous solutions of platinic chloride led to very unstable, ill-defined products, from which crystalline bistrialkylstibinedichloro-platinums could not be isolated in a state of purity. Analysis of the higher homologue showed that the product had undergone extensive decomposition.

II. *Palladium Series.*

Bistrimethylstibinedichloropalladium (VI).—On adding trimethyl-stibine to an aqueous solution of palladous chloride cooled in a freezing mixture, an orange-yellow deposit separated, the colour of which persisted at the low temperature. As the temperature rose to normal the product became lemon-yellow and retained this colour on drying. The product was soluble in alcohol or chloro, form, but insoluble in water or ether. On prolonged warming, it decomposed without melting, liberating metallic palladium : 0·1059 gave 0·0570 CO_2, 0·0352 H_2O, C = 14·60, H = 3·69; 0·0568 gave 0·0256 PdSb, 0·0323 AgCl, Pd = 21·09, Cl = 14·01; M in chloroform = 515. $C_6H_{18}Cl_2Sb_2Pd$ requires C = 14·2, H = 3·58, Pd = 21·0, Cl = 13·95%; M = 508.

Tetrakistrimethylstibinepalladous Chloride (VII).—The more soluble tetrakis compound formed in the preceding preparation separated from the aqueous filtrate in well-defined, golden-orange needles contaminated with trimethylstibine dichloride, the latter being removed by ether. The tetrakis compound was readily soluble in water, but was decomposed by boiling, although it was more stable than the bis compound : 0·0957 gave 0·0595 CO_2, 0·0292 H_2O, C = 17·00, H = 3·42; 0·0616 gave 0·0079 Pd, Pd = 12·80. $C_{12}H_{36}Cl_2Sb_4Pd$ requires C = 17·05, H = 4·28, Pd = 12·6%.

This tetrakis compound was also obtained by the action of excess of trimethylstibine on bistrimethylstibinedichloropalladium, although the yield was diminished by reduction of a portion of the palladium present in the latter reagent. The stability of the resulting product was increased materially by keeping it in the dark throughout its preparation and separation. When boiled for some time with dilute hydrochloric acid or a large excess of chloroform, this tetrakis derivative was converted into a lemon-yellow substance (VIII) soluble in water or organic media and distinctly acidic to bromophenol-blue. Unlike the other pallado-derivatives (VI and VII), this product was stable on keeping in the air and gave a light brown precipitate with cæsium hydroxide : 0·1121 gave 0·0490 Sb_2S_3 and 0·0321 Pd, Sb = 31·1, Pd = 28·6. $C_3H_{10}Cl_3SbPd$ requires Sb = 32·03, Pd = 28·07%.

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XXX.—*αγ-Dialdehydopropane-ββ-dicarboxylic   Acid and αγ-Dialdehydopropane-β-carboxylic Acid.*

By WILLIAM HENRY PERKIN, jun., and HERBERT SHEPPARD PINK.

THIS communication is a continuation of the work of Perkin and Sprankling (J., 1899, **75**, 11), who showed that ethyl acetalmalonate, obtained when ethyl sodiomalonate is heated with bromoacetal, yields, on hydrolysis, acetalmalonic acid and that this acid, when heated with water at 180°, loses carbon dioxide with the formation of β-aldehydopropionic acid :

$$(EtO)_2CH\cdot CH_2\cdot CH(CO_2Et)_2 \longrightarrow (EtO)_2CH\cdot CH_2\cdot CH(CO_2H)_2$$
$$\longrightarrow CHO\cdot CH_2\cdot CH_2\cdot CO_2H.$$
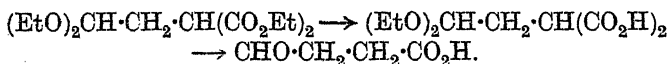
The oxidation of the latter acid to succinic acid, its reduction to butyrolactone, and its conversion into terephthalic acid by treatment with alkali were described.   It is now shown that the potassium derivative of ethyl acetalmalonate reacts with bromoacetal with the formation of ethyl diacetalmalonate (A) and that this ester, on hydrolysis with baryta, yields diacetalmalonic acid, $(EtO)_2CH\cdot CH_2\cdot C(CO_2H)_2\cdot CH_2\cdot CH(OEt)_2.$

When the ester (A) is left in contact with N-hydrochloric acid in the cold, it is converted into the *ester* of *αγ-dialdehydopropane-ββ-dicarboxylic acid*, $CHO\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CHO$, but if concentrated hydrochloric acid is employed, further hydrolysis takes place and *αγ-dialdehydopropane-ββ-dicarboxylic acid* is produced.   Apart from the method of synthesis, the constitution of this acid is demonstrated by the facts that it is converted on reduction into bis-γ-butyrolactone-αα-spiran (I) which Leuchs and Gieseler (*Ber.*, 1912, **44**, 2114) obtained by the action of ethylene bromoacetate on ethyl sodiomalonate and that, on oxidation, it yields propane-αββγ-tetracarboxylic acid (II), which, at its melting point, is decomposed with elimination of carbon dioxide and formation of tricarballylic acid (compare Bischoff, *Ber.*, 1896, **29**, 267).

(I.) $\begin{matrix} CH_2\cdot CH_2 \\ | \qquad \quad \\ O \text{———} CO \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} CH_2\cdot CH_2 \\ \qquad \quad | \\ CO\text{———}O \end{matrix}$ $CO_2H\cdot CH_2\cdot C(CO_2H)_2\cdot CH_2\cdot CO_2H$ (II.)
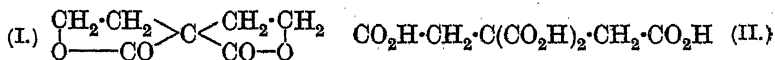
When αγ-dialdehydopropane-ββ-dicarboxylic acid is heated with water at 180°, it is decomposed with elimination of carbon dioxide and formation of *αγ-dialdehydopropane-β-carboxylic acid*,

$$CHO\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CHO.$$

EXPERIMENTAL.

Ethyl Diacetalmalonate.—The ethyl acetalmalonate required for the preparation of this substance was obtained by adding ethyl

malonate (100 g.) and bromoacetal (80 g.) to sodium (14·2 g.) dissolved in alcohol (200 c.c.). The mixture was heated in an autoclave fitted with a mechanical stirrer for 4 hours, the temperature of the surrounding oil-bath being kept at 180°. The product was worked up as described in the previous communication (J., 1899, **75**, 13), and the ester (72 g.) distilled at 163—165°/20 mm. In the preparation of the diacetal derivative, potassium (8 g.) is melted under boiling toluene (50 c.c.), pulverised by shaking, cooled, and ethyl acetalmalonate (55 g.) added very gradually. A vigorous action takes place and if the ester is added too rapidly, the heat generated is sufficient to raise the toluene to the boiling point and the solution turns brown. When all the ethyl acetalmalonate has been introduced and the last traces of metal have disappeared, bromo-acetal (40 g.) is added and four such portions are united and heated in the autoclave during 6 hours with constant stirring, the temperature of the oil-bath being maintained at 200°. After standing over-night, the product is transferred to flasks, the toluene removed under reduced pressure, the residue mixed with water and ether, the ethereal extract well washed, dried over anhydrous potassium carbonate, and the ether distilled off. The distillation is continued under reduced pressure, when unchanged ethyl acetalmalonate (80 g.) comes over at 140—170°/20 mm.; the thermometer then rises rapidly to 187°, between which temperature and 200° the main portion of the ethyl diacetalmalonate passes over; there is a further fraction at 200—250° which has not been examined. On redis-tillation, *ethyl diacetalmalonate* is obtained as a colourless, rather viscid oil, b. p. 192—196°/18 mm., $d_{22°}^{22°}$ 1·031 (Found : C = 58·3; H = 9·2. $C_{19}H_{26}O_8$ requires C = 58·2; H = 9·2%).

Hydrolysis.—(i) By Alkali. The ester (5 g.) was mixed with a methyl-alcoholic solution of barium hydroxide (32 c.c. of a solution of 16 g. of $Ba(OH)_2,8H_2O$ in 100 c.c. of methyl alcohol = 25% excess) and boiled on the steam-bath for 4 hours. Water (10 vols.) was then added, the whole saturated with carbon dioxide, and the filtrate from the barium carbonate concentrated on the steam-bath, but the salt did not crystallise. On evaporation to dryness, a pale yellow, brittle salt remained which is moderately soluble in water (Found : Ba = 31·0. $C_{15}H_{26}O_8Ba$ requires Ba = 29·1%). The powdered barium salt (5 g.) was mixed with a little water, and slightly less than the calculated quantity (21 c.c.) of N-sulphuric acid added with vigorous stirring. After standing over-night, the whole was filtered, the filtrate extracted repeatedly with pure ether, the ethereal solution dried over anhydrous magnesium sulphate, and the ether allowed to evaporate, when *diacetalmalonic acid* was left as a pale, viscid syrup which showed no tendency to crystallise.

After remaining for 3 days in a vacuum desiccator over solid potassium hydroxide, this was analysed (Found : C = 53·3 ; H = 8·3. $C_{15}H_{28}O_8$ requires C = 53·6 ; H = 8·3%. On titration with N/10-alcoholic potassium hydroxide, 0·22 neutralised 0·0533 KOH, whereas this amount of a dibasic acid, $C_{15}H_{28}O_8$, should neutralise 0·0524 KOH).

(ii). By Concentrated Hydrochloric Acid. Ethyl diacetalmalonate (10 g.) was well shaken with concentrated hydrochloric acid (30 c.c.), when complete solution took place, and, after 24 hours, the rather dark liquid was diluted with water, filtered from a little tarry matter, and evaporated to a small bulk under reduced pressure, the temperature not being allowed to rise above 30°. After further evaporation over sulphuric acid in a vacuum desiccator, a pale brown syrup resulted and this was mixed with water and again evaporated, the operation being repeated several times. The syrup remained as such for 7 weeks and then suddenly crystallised and the mass was drained on porous porcelain and crystallised from water, from which it separated in colourless prisms (Found : C = 44·7 ; H = 4·5. $C_7H_8O_6$ requires C = 44·7 ; H = 4·3%). αγ-*Dialdehydopropane*-ββ-*dicarboxylic acid* melts at 122° with decomposition and is readily soluble in water, alcohol, or acetone, sparingly so in ether, and almost insoluble in petroleum, benzene, chloroform, or carbon tetrachloride. On titration, 0·1562 neutralised 0·0665 NaOH, whereas this amount of a dibasic acid, $C_7H_8O_6$, should neutralise 0·0664 NaOH. A neutral solution of the ammonium salt gives, with silver nitrate, a white precipitate which rapidly darkens and silver is deposited.

The *di*-p-*nitrophenylhydrazone* separated as a yellow, crystalline precipitate when the aqueous solution of the acid (0·6 g.) was mixed with *p*-nitrophenylhydrazine (0·85 g.), dissolved in dilute acetic acid, and separated from alcohol in glistening plates, m. p. 156° (decomp.) (Found : N = 18·2. $C_{19}H_{18}O_8N_6$ requires N = 18·3%). The *ethyl* ester was obtained when ethyl diacetalmalonate (15 g.) was well shaken with N-hydrochloric acid (30 c.c.) and, after remaining for 24 hours, the whole was several times extracted with ether, the extract washed with sodium carbonate, dried over potassium carbonate, and distilled, when the ester passed over at 174—178°/18 mm. The p-*nitrophenylhydrazone*, prepared in dilute acetic acid solution, crystallised from alcohol as a microcrystalline powder, m. p. 170° (Found : N = 16·2. $C_{23}H_{26}O_8N_6$ requires N = 16·3%).

Reduction of αγ-*Dialdehydopropane*-ββ-*dicarboxylic Acid.*—The dibasic acid (4 g.), dissolved in water (75 c.c.), was mixed with sodium bicarbonate (15 g.) and treated with sodium amalgam (150 g. of 4%) in a flask fitted with a mechanical stirrer and cooled in ice, the

reduction being complete in about 8 hours. The alkaline solution was acidified with dilute sulphuric acid (10 g.) in water (20 c.c.), concentrated on the steam-bath, repeatedly extracted with chloroform, the extract dried over anhydrous magnesium sulphate, and the chloroform allowed to evaporate. The colourless, crystalline residue separated from water in plates, m. p. 109—110°, and was evidently identical with bis-γ-butyrolactone-αα-spiran described by Leuchs and Gieseler (*loc. cit.*).

Oxidation of αγ-Dialdehydopropane-ββ-dicarboxylic Acid.—The acid (5 g.), dissolved in water (20 c.c.), was mixed with potassium dichromate (5·2 g.) in sulphuric acid (6·9 g.) and water (75 c.c.) and allowed to stand for 12 hours, during which the colour changed to green. The product, evaporated on the steam-bath to 50 c.c., was extracted with ether, the extract dried over anhydrous magnesium sulphate, and the ether allowed to evaporate over sulphuric acid. The oily residue remained for weeks without crystallising, but did so rapidly when a crystal of propane-αββγ-tetracarboxylic acid was introduced. After contact with porous porcelain, the substance separated from ether in needles, melted at 151° with decomposition into carbon dioxide and tricarballylic acid, and was thus identified with propane-αββγ-tetracarboxylic acid.

αγ-Dialdehydopropane-β-carboxylic Acid.—This acid was obtained when αγ-dialdehydopropane-ββ-dicarboxylic acid (4 g.), dissolved in water (16 c.c.), was heated in a sealed tube at 180° for 4 hours. On opening the tube, carbon dioxide escaped and the solution, evaporated in a vacuum over sulphuric acid, deposited a syrup which, even on long standing, did not crystallise (Found : $C = 49·5$; $H = 5·5$. $C_6H_8O_4$ requires $C = 50·0$; $H = 5·5\%$). The *di-p-nitrophenylhydrazone*, obtained by adding a solution of *p*-nitrophenylhydrazine in dilute acetic acid to the aqueous solution of the acid and heating for an hour on the steam-bath, is a yellow, amorphous powder sparingly soluble in the usual solvents. The substance could not be recrystallised and was purified by extraction with hot alcohol and then with ether, when the residue melted at about 198° (decomp.) (Found : $N = 20·3$. $C_{18}H_{18}O_6N_6$ requires $N = 21·3\%$).

XXXI.—*New Synthesis of the Meconines.*

By GEORGE ALFRED EDWARDS, WILLIAM HENRY PERKIN, jun., and FRANCIS WILBERT STOYLE.

THIS communication is concerned with a new and direct method for the synthesis of meconine (I) and *m*-meconine (III), and an indirect one for that of ψ-meconine (II), since this substance is quite easily prepared from meconine.

Meconine (I.) ψ-*Meconine* (II.)   *m*-*Meconine* (III.)
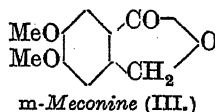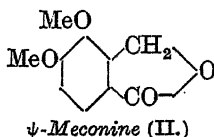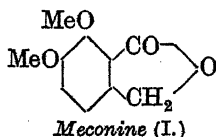
The direct substitution of the group $-CH_2 \cdot OH$ into the benzene nucleus has been carried out in a variety of ways. Benzene itself, when treated with *s*-dichlorodimethyl ether in presence of zinc chloride, gives some benzyl chloride (Stephen, Gladding, and Short, *J.*, 1920, **117**, 570), whilst phenols and their ethers condense with formaldehyde in presence of cold aqueous alkali to yield the corresponding benzyl alcohols (Manasse, *Ber.*, 1894, 27, 2411; Lederer, *J. pr. Chem.*, 1894, [ii], 50, 225). We have found that the veratric acids do not condense at all readily either with *s*-dichlorodimethyl ether or with cold aqueous formaldehyde, but on boiling with an excess of formaldehyde and concentrated hydrochloric acid the corresponding meconine is formed in moderately good yield according to the scheme

$$(MeO)_2C_6H_3 \cdot CO_2H + HCHO \longrightarrow (MeO)_2C_6H_2{<}_{CH_2 \cdot OH}^{CO_2H} \longrightarrow$$
$$(MeO)_2C_6H_2{<}_{CH_2}^{CO-}{>}O.$$
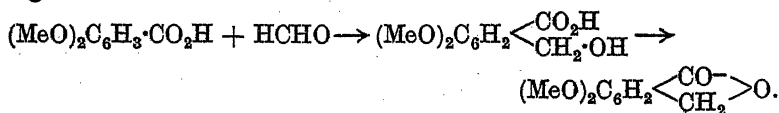
Meconine, which was originally prepared synthetically in very poor yield by the condensation of *o*-veratric acid with chloral (Fritsch, *Annalen*, 1898, **301**, 51), has now been obtained in 25—30% yields by the above-mentioned method, the formaldehyde unexpectedly substituting entirely in the position ortho to the carboxyl group, as was shown by the identity of the only product isolated with the substance produced by the reduction of opianic acid (IV).

Since meconine on oxidation with manganese dioxide and dilute sulphuric acid is converted into opianic acid (IV), this new synthesis of meconine is also a synthesis of opianic acid, an acid which has not previously been obtained synthetically (compare Perkin and Fargher, *J.*, 1921, **119**, 1724). It further provides a synthesis of

H 2

hemipinic acid, since this substance is produced on oxidation with potassium permanganate.

$$
\begin{array}{ccc}
\underset{\text{MeO}}{\overset{\text{CO}_2\text{H}}{\underset{\text{MeO}}{\bigcirc}}}\text{CHO} & \underset{\text{MeO}}{\overset{\text{MeO}}{\bigcirc}}\overset{\text{CH}_2\cdot\text{OH}}{\underset{\text{CO}_2\text{H}}{}} & \underset{\text{MeO}}{\overset{\text{MeO}}{\bigcirc}}\overset{\text{CHO}}{\underset{\text{CO}_2\text{H}}{}} \\
\text{(IV.)} & \text{(V.)} & \text{(VI.)}
\end{array}
$$
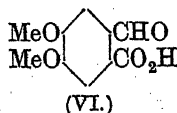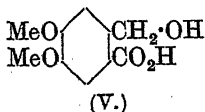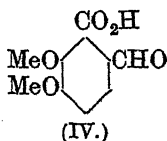
An indirect synthesis of ψ-meconine (II) is completed by converting the hemipinic acid, obtained as above, into its anhydride, $(\text{MeO})_2\text{C}_6\text{H}_2\underset{\text{CO}}{\overset{\text{CO}}{<}}>\text{O}$, by dehydration with acetyl chloride, and reducing the product with zinc dust and acetic acid (compare Salomon, *Ber.*, 1887, **20**, 889). Attempts to prepare ψ-opianic acid by oxidation of the ψ-meconine were all unsuccessful, the acid first formed being more easily oxidised than the ψ-meconine itself. Salomon (*loc. cit.*) states that he was unable to bring about this oxidation.

m-Meconine (III), first obtained by Perkin (J., 1916, **109**, 815) from the degradation products of cryptopine derivatives, is similarly produced by the condensation of veratric acid with formaldehyde in presence of concentrated hydrochloric acid, and the synthetic product is in every way identical with the *m*-meconine obtained by Perkin. The lactone ring of this substance is readily opened by alkalis, and on neutralising the cooled solution of the resulting salt with acetic acid, 4 : 5-dimethoxy-2-carboxybenzyl alcohol (V) slowly separates. Strong mineral acids rapidly transform this into the lactone, as does heating it to its melting point or boiling its aqueous solution.

m-Opianic acid (VI), required in the laboratory for synthetic work, is very difficult to obtain, and it was hoped that it might be possible to prepare it from *m*-meconine by oxidation. But although treatment with manganese dioxide and dilute sulphuric acid yielded sufficient *m*-opianic acid for identification, the method in its present form is valueless for the preparation of any quantity of material.

On the other hand, *m*-hemipinic acid in moderately good yield is obtained by the oxidation of *m*-meconine with alkaline permanganate, and this may prove the most convenient method for the preparation of this acid.

Attempts were also made to obtain the methylene ether of 4 : 5-dihydroxyphthalide by the condensation of piperonylic acid with formaldehyde, but even after long boiling, most of the acid was recovered unchanged, only a small yield of an easily oxidisable substance of high molecular weight being produced.

o-*Veratric Acid.*—The preparation of this acid by the oxidation of o-veratraldehyde was best carried out in the following way. The aldehyde (30 g.) was kept boiling under a reflux condenser with water (300 c.c.) and potassium bicarbonate (35 g.) while a hot solution of potassium permanganate (22 g.) in water was added slowly. The cooled and filtered solution, on acidification, yielded o-veratric acid, m. p. 120—122°.

Meconine (I).—o-Veratric acid (10 g.), formaldehyde solution (25 c.c. of 40%), and concentrated hydrochloric acid (40 c.c.) were boiled together under reflux for 15—20 minutes, when the solution had turned brown and a dark gum had separated. The hot solution was filtered, cooled, and diluted with water, when a mixture of meconine with unchanged acid crystallised out. The solid was washed with sodium carbonate solution to remove the acid, and the meconine (2·5—3 g.) was crystallised from hot water, being obtained in colourless prisms, m. p. 102°. Its identity with the product of the reduction of opianic acid with sodium amalgam was shown by a variety of methods (Found: $C = 62·0$; $H = 5·2$. Calc. for $C_{10}H_{10}O_4$, $C = 61·6$; $H = 5·1\%$).

Opianic Acid (IV).—Meconine (3 g.) was boiled for 3 hours under reflux with dilute sulphuric acid (50 c.c. of 20% solution) and finely powdered manganese dioxide (10 g.). The resulting solution, on cooling and standing, deposited crystals of opianic acid in a practically pure state and in nearly theoretical yield. After a further recrystallisation from hot water, the acid was obtained as colourless prisms, m. p. 146°. It was shown to be identical in every respect with the opianic acid obtained by the oxidation of narcotine with manganese dioxide (Found: $C = 57·2$; $H = 4·9$. Calc. for $C_{10}H_{10}O_5$, $C = 57·1$; $H = 4·8\%$).

Hemipinic Acid.—This acid was best obtained as follows. Opianic acid (10 g.), water (100 c.c.), and lead dioxide (30 g.) were kept at 100° on a water-bath while dilute sulphuric acid was slowly run in. When the evolution of carbon dioxide became rapid, the mixture was cooled, a little more sulphuric acid added, the solution filtered from lead sulphate and excess lead dioxide, and evaporated to small bulk. The hemipinic acid separated on cooling in a hydrated crystalline state, and the anhydrous acid was obtained by heating it at 100° for some time. The amorphous product (7—8 g.) melted at 177°.

Hemipinic anhydride is most conveniently prepared as follows. The acid is heated under reflux with excess of acetyl chloride for 1 hour, when the solution is evaporated to small bulk, and the

anhydride allowed to crystallise from the residue. It is thus obtained as glistening needles, m. p. 168°.

Veratric acid, the preparation of which is not, apparently, described in detail in the literature, is best obtained by slowly adding potassium permanganate (34 g.) in warm water to a constantly stirred mixture of veratraldehyde and water (50 g. in 300 c.c.) kept at 50—60°, a current of carbon dioxide being passed through the solution the whole time. The filtered and cooled solution is extracted with ether to remove any unchanged aldehyde, and the product thrown out by acidification. Veratric acid (50 g.) is thus obtained in a nearly pure, semi-gelatinous state, and without further purification melts at 179°.

m-*Meconine.*—Veratric acid (50 g.) was heated on a water-bath for 12 hours with formaldehyde (55 c.c. of 40% solution) and concentrated hydrochloric acid (200 c.c.). The product was cooled rapidly, diluted with its own bulk of water, and shaken violently until the emulsion formed deposited a gummy substance on the walls of the vessel, leaving a clear solution. The latter, after being filtered and allowed to stand, slowly deposited m-meconine (9—15 g.) as a brown, crystalline powder. After washing with sodium carbonate solution, it was recrystallised from dilute alcohol, when it separated as colourless needles, m. p. 155—157°. It was identical with the substance obtained by Perkin (*loc. cit.*) by the reduction of m-opianic acid with sodium amalgam.

Further quantities of the lactone were obtained by extracting the resinous substance left clinging to the walls of the reaction vessel with hot caustic soda solution, boiling the filtrate with animal charcoal, and acidifying with hydrochloric acid. The substance which separated on standing recrystallised from aqueous alcohol with a brown colour, but melted at the same temperature as the colourless crystals (Found : C = 61·7; H = 5·0. Calc. for $C_{10}H_{10}O_4$, C = 61·8; H = 5·1%).

4 : 5-*Dimethoxy-2-carboxybenzyl Alcohol* (V).—m-Meconine was dissolved in the minimum amount of hot caustic soda solution, and the cooled product was just acidified with acetic acid. On standing, the hydroxy-acid separated as clusters of minute needles melting indefinitely at 146—149°. The product is very much more soluble in water than m-meconine; but if the solution is kept boiling for a short time m-meconine separates as fine needles.

Oxidation of m-*Meconine.*—m-Meconine was boiled for 4 hours with manganese dioxide and dilute sulphuric acid in the same proportions as those used in the oxidation of meconine. On filtering and cooling the product, about one-third of the m-meconine separated unchanged. The mother-liquor, after being made

alkaline with sodium carbonate, was filtered and the manganese in solution was thus removed as carbonate. The acidified solution was evaporated to dryness in a vacuum, the dry residue extracted with boiling absolute alcohol, and the solution evaporated. The product was taken up in a little boiling water, and one or two drops of phenylhydrazine were added. After the solution had boiled for a short time, the phenylhydrazone of m-opianic acid separated as white flocks, and after recrystallisation from alcohol became colourless at 173—176° and melted at 228°. This behaviour was shown by Perkin and Fargher (J., 1921, 119, 1743) to be characteristic of m-opianic acid, and a mixed melting point with some of the phenyl-m-opiazone (m. p. 228°) prepared by them established the identity.

m-*Hemipinic Acid.*—A solution of m-meconine in a slight excess of aqueous caustic soda was saturated with carbon dioxide, and a little sodium bicarbonate added. The calculated amount of potassium permanganate for the oxidation having been added, the mixture was heated on the water-bath until the colour of the permanganate had been removed, a current of carbon dioxide being passed through the whole time. The filtered and acidified solution was evaporated to small bulk, and the resulting liquid deposited m-hemipinic acid as yellow crystals, m. p. 203° (decomp.). This was shown to be identical with the acid obtained by Perkin and Fargher (*loc. cit.*).

XXXII.—*Method of Measuring the Reduction Potentials of Quinhydrones.*

By EINAR BIILMANN, A. LANGSETH JENSEN, and KAI O. PEDERSEN.

IT has been pointed out by one of us (*Trans. Faraday Soc.*, 1923, 19, 676) that the reduction potential of a quinhydrone can be determined by measuring the potential of an electrode containing, for instance, the *hydroquinone of one quinhydrone* in a solution of the *quinone of another quinhydrone with a known reduction potential*, that is, without preparing the quinhydrone itself or both its con-

stituents. In this paper, the theory of the method is described and some quantitative results are detailed.

Let A, AH_2, and (A,AH_2) be a certain quinone, hydroquinone, and quinhydrone, respectively, and let B, BH_2, and (B,BH_2) be another, similar series. Then, if a solution of the hydroquinone, AH_2, be mixed with a solution of the quinone, B, AH_2 will be partly oxidised to the quinone, A, at the expense of B, which will be partly reduced to its corresponding hydroquinone, BH_2. Starting with equimolecular quantities of AH_2 and B, the reaction may be written

$$aAH_2 + aB \longrightarrow (a - x)AH_2 + xA + (a - x)B + xBH_2 \quad . \quad (1)$$
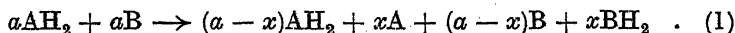
and the equilibrium set up must be such that the reduction potential π (as measured against a hydrogen electrode) of the mixture $(a - x)AH_2 + xA$ is equal to the reduction potential of the mixture $(a - x)B + xBH_2$.

We have now four electrolytic chains to consider

(a) $\mathrm{Pt} \Big|^{(a - x) \cdot mAH_2}_{x \cdot mA}$; electrolyte; (A,AH_2) Pt
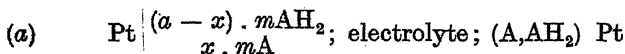
with an $E.M.F.$ $\phi' = \dfrac{RT}{nF} \log_e \dfrac{x}{a - x} = K \log_{10} \dfrac{x}{a - x}$.   . (2)

(b) the similar chain

$$\mathrm{Pt} \Big|^{x \cdot mBH_2}_{(a - x) \cdot mB}\text{; electrolyte; } (B,BH_2) \Big| \mathrm{Pt}$$
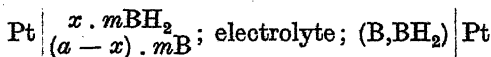
for which

$$\phi = \dfrac{RT}{nF} \cdot \log_e \dfrac{a - x}{x} = -K \log_{10} \dfrac{x}{a - x} \quad . \quad . \quad (3)$$

so that $\phi = -\phi'$;

(c) the quinhydrone electrode

$$\mathrm{Pt} \mid (A,AH_2); \ H_2 \mid \mathrm{Pt}$$

with the reduction potential π_0';

and (d) the quinhydrone electrode

$$\mathrm{Pt} \mid (B,BH_2); \ H_2 \mid \mathrm{Pt}$$
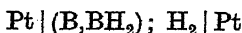
with the reduction potential π_0.

Now, for equilibrium we must have

$$\pi = \pi_0' - \phi = \pi_0 + \phi$$

$i.e.,$ $\pi_0' = 2\pi - \pi_0 = 2\phi + \pi_0$.   .   .   . (4)

where π is the voltage both of the chain

$$\mathrm{Pt} \ ^{(a - x) \cdot mAH_2}_{x \cdot mA}; \ H_2 \ \mathrm{Pt}$$

and of the chain

$$\mathrm{Pt} \ ^{(a - x) \cdot mB}_{x \cdot mBH_2}; \ H_2 \Big| \mathrm{Pt}$$
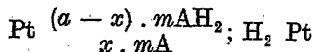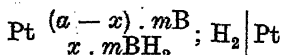
That is to say, the reduction potential, π_0', of the quinhydrone (A, AH_2) can be determined by measuring

(i) the potential, π, of a mixture of the hydroquinone AH_2 with an equimolecular quantity of the quinone B (or conversely) to a hydrogen electrode.

or (ii) the potential, ϕ, of this mixture to the quinhydrone electrode (B, BH_2).

<p style="text-align:center">Fig. 1.</p>
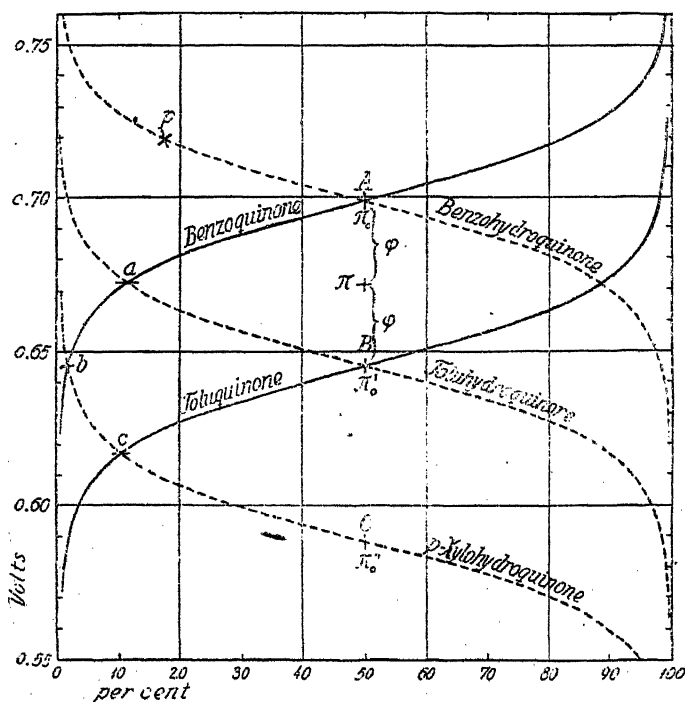
In both cases, we require to know the reduction potential, π_0, of the quinhydrone (B, BH_2) electrode; and obviously the electrolyte, the temperature, and the hydrogen pressure (1 atm.) must be the same in all the electrodes.

Combining equations (3) and (4), we get

$$\pi_0' - \pi_0 = 2\phi = 2K \log_{10}\{x/(a - x)\} =$$
$$\text{(at } 25°\text{) } 0{\cdot}0591 \log_{10}\{x/(a - x)\},$$

from which equation x may be calculated when π_0 and π_0' have been determined.

Taking the reduction potentials at 25° for benzoquinhydrone, toluquinhydrone, and p-xyloquinhydrone as 0·6990, 0·6454, and

0·5886 volt, respectively, the following values for the percentage of quinhydrone unchanged in equimolecular mixtures with quinones are obtained :

Mixture.	% Hydroquinone unchanged.
Benzoquinone + Toluhydroquinone	12·4
Benzoquinone + p-Xylohydroquinone	1·4
Toluquinone + p-Xylohydroquinone	9·1

Two sources of error must be briefly mentioned. First, the position of the equilibrium markedly affects the accuracy attainable. Fig. 1 shows the relation between the composition of the solution and the potential referred to a hydrogen electrode at 25°. Thus, p denotes the potential (0·72 volt) of a mixture of 18·5% of benzohydroquinone and 81·5% of benzoquinone. Similarly A, B, and C denote the potentials of the three quinhydrones. Now the potential of the equilibrium mixture of toluhydroquinone and benzoquinone is given by point a (the intersection of the corresponding curves), and it is obvious from the figure that the farther this point is removed from the centre line ABC, the more rapidly will the potential change with composition, and the less accurate will be the results.

The second source of error is due to the inequality of the dissociation constants * of the various quinhydrones. At 25°, the dissociation constant of benzoquinhydrone is 0·224, whilst for toluquinhydrone it is 0·095 (Biilmann, *Ann. Chim.*, 1921, [ix], 15, 151). But by comparing the values obtained by the " mixture " method with those obtained directly by La Mer (*J. Amer. Chem. Soc.*, 1922, 44, 1954) and one of us (Biilmann, *loc. cit.*) and also in this research, it is seen that satisfactory agreement is obtained,

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* Let the initial concentrations of A and BH_2 be, and the stoicheiometric amounts of the quinones and hydroquinones at equilibrium (as assumed in equation 1) be AH_2, $a - x$; A, x; BH_2, x; and B, $a - x$.

If the concentrations of undissociated quinhydrones AH_2,A and BH_2,B are a and β respectively, the concentrations of the dissociated components will be AH_2, $a - x - a$; A, $x - a$; BH_2, $x - \beta$; and B, $a - x - \beta$.

In the equilibrium set up, the potentials of the mixtures of A and AH_2 and of B and BH_2 against the corresponding two quinhydrones are (equation 2) $\phi_A = K \log_{10} \dfrac{x - a}{a - x - a}$ and $\phi_B = K \log_{10} \dfrac{x - \beta}{a - x - \beta}$ respectively.

If, as supposed, $\pi_0' - \pi_0 = 2\phi$, we have $\phi_A = \phi_B$ and, consequently, $(x - a)/(a - x - a) = (x - \beta)/(a - x - \beta)$ or $2x(a - \beta) = a(a - \beta)$.

Consequently, the supposed relation between the potential of the mixture and the reduction potentials of the single quinhydrones is strictly exact if $a = \beta$, *i.e.*, the two quinhydrones have the same dissociation constants [as $k_A = (x - a)(a - x - a)/a$; $k_B = (x - \beta)(a - x - \beta)/\beta$], or if $x = a/2$, *i.e.*, their reduction potentials are identical.

especially when the sparing solubility of the materials dealt with is considered.

In some cases, the equilibrium potential was reached almost instantaneously; in others, it was necessary to wait for some hours before measurement.

Table I records the experimental results.

TABLE I.

Reduction Potentials of Quinhydrones.

Composition of quinhydrone.	π_0 measured in mixture.		Other determinations of π_0 at 25°.
	At 18°.	At 25°.	
$C_6H_3Me(OH)_2,C_6H_3MeO_2$	0·6496	0·6444	0·6454 *
$C_6H_2Me_2(OH)_2,C_6H_2Me_2O_2$	—	0·5893	0·5886
$C_6H_3Cl(OH)_2,C_6H_3ClO_2$	0·7178	0·7124	0·7125 †
$C_6H_3Br(OH)_2,C_6H_3BrO_2$	0·7174	0·7120	0·7151 †
$1:4\text{-}Cl_2{:}C_6H_2(OH)_2,C_6H_2Cl_2O_2$	0·7280	0·7230	
$1:4\text{-}Br_2{:}C_6H_2(OH)_2,C_6H_2Br_2O_2$	0·7280	0·7228	
$1:4\text{-}ClMe{:}C_6H_2(OH)_2,C_6H_2MeClO_2$	—	0·6542	0·6566
$1:4\text{-}BrMe{:}C_6H_2(OH)_2,C_6H_2MeBrO_2$	—	0·6564	0·6591
$C_6HMe_2Cl(OH)_2,C_6HMe_2ClO_2$	—	0·5949	0·5918

* Biilmann, *loc. cit.*　　　　　　　† La Mer, *loc. cit.*

EXPERIMENTAL.

Toluhydroquinone.—The toluhydroquinone was recrystallised from toluene immediately before the solution was made up. Equal volumes of $0·01M$-solutions of toluhydroquinone and benzoquinone in $0·1N$-hydrochloric acid were mixed and the potentials measured against a benzoquinhydrone electrode, blank platinum electrodes being used.

TABLE II.

$$-Pt\left|\begin{array}{l}\text{Toluhydroquinone, }0·005M\\ \text{Benzoquinone, }0·005M\end{array}\right.;\ \frac{\text{HCl}}{0·1N};\ \text{Benzoquinhydrone}\left|Pt+\right.$$

Temp.	25·4°.		18°.	
Minutes	30	60	150	180
Volt, I *	0·0273	0·0273	0·0274	0·0274
„ II *	0·0274	0·0274	0·0275	0·0275
	$\pi_{25°} = 0·6444.$		$\pi_{18°} = 0·6496.$	

* Duplicate electrodes.

p-Xylohydroquinone.—The potentials were measured as above, but the electrolyte was $0·1N$-sulphuric acid saturated with carbon dioxide, and all the operations were carried out in an atmosphere of this gas.

H* 2

TABLE III.

$-Pt$ $\begin{array}{l}\text{Xylohydroquinone, } 0\cdot00125M\\\text{Toluquinone, } 0\cdot00125M\end{array}$; $\begin{array}{l}H_2SO_4\\0\cdot1N\end{array}$; Benzoquinhydrone Pt$+$

25·4°

Temp. Minutes	25	60	105	135	165	195	1200	1290	1460
Volt, I	0·0689	0·0775	0·0802	0·0809	0·0811	0·0813	0·0820	0·0821	0·0821
„ II	0·0702	0·0773	0·0792	0·0803	0·0807	0·0810	0·0822	0·0822	0·0823

$\pi_{25°} = 0\cdot5893$.

Solution prepared from equimolecular quantities of p-xylohydroquinone and p-xyloquinone in $0\cdot1N$-sulphuric acid with carbon dioxide treatment as before.

TABLE IV.

$-Pt$ $\left|\begin{array}{l}p\text{-Xylohydroquinone, } 0\cdot00125M\\p\text{-Xyloquinone, } 0\cdot00125M\end{array}\right.$; $\begin{array}{l}H_2SO_4\\0\cdot1N\end{array}$; Benzoquinhydrone Pt$+$

Temp.	25·6°.				18°.	
Minutes	5	45	95	145	185	385
Volt, I	0·1101	0·1104	0·1104	0·1104	0·1103	0·1104
„ II	0·1102	0·1105	0·1105	0·1105	0·1105	0·1106

$\pi_{25°} = 0\cdot5886$. $\pi_{18°} = 0\cdot5940$.

Without the carbon dioxide treatment, constant potentials could not be obtained. The potentials, measured against the benzoquinhydrone electrode, of a similar electrode prepared without the carbon dioxide treatment are recorded in Table V, and it will be seen that the potentials slowly rise until, after 20 hours, they are practically identical with those in Table IV. This may be due to catalytic oxidation of the hydroquinone on the surface of the platinum, the potential reaching the value in Table IV only when the solution in the electrode vessel is thoroughly mixed by diffusion.

TABLE V.

$-Pt$ $\left|\begin{array}{l}p\text{-Xylohydroquinone, } 0\cdot00125M\\p\text{-Xyloquinone, } 0\cdot00125M\end{array}\right.$; $\begin{array}{l}H_2SO_4\\0\cdot1N\end{array}$; Benzoquinhydrone $\left|\right.$Pt$+$

25·4°.

Temp. Minutes	15	60	120	150	1120	1270
Volt, I	0·1072	0·1090	0·1099	0·1100	0·1101	0·1101
„ II	0·1070	0·1093	0·1098	0·1099	0·1103	0·1103

$\pi_{25°} = 0\cdot5888$.

Monochlorohydroquinone.—Benzoquinone (10 g.) was heated with 100 c.c. of concentrated hydrochloric acid for ¾ hour on the steam-bath (Wöhler, *Annalen*, 1844, **51**, 155), the solution cooled, diluted with water, and extracted with ether. The residue after evaporation of the ether had m. p. 103° when crystallised twice from chloroform, and 105—105·5° (constant) when crystallised

subsequently from carbon tetrachloride.   Levy and Schultz quote 106° (*ibid.*, 1881, **210**, 138), and Schultz quotes 103—104° (*Ber.*, 1882, **15**, 654).

TABLE VI.

−Pt Benzoquinhydrone; $\dfrac{\text{HCl}}{0\cdot 1N}$; $\begin{array}{l}\text{Monochlorohydroquinone, } 0\cdot 005M\\ \text{Benzoquinone, } 0\cdot 005M\end{array}$ | Pt +

Temp.	25·4°.			18°.		18°.*
Minutes	15	30	60	120	180	
Volt, I	0·0068	0·0068	0·0068	0·0067	0·0067	0·0066
„ II	0·0067	0·0067	0·0067	0·0066	0·0066	0·0066

$$\pi_{25°} = 0\cdot 7124. \qquad\qquad \pi_{18°} = 0\cdot 7178.$$

* After dilution with 3 vols. of 0·1*N*-HCl.

Monobromohydroquinone was prepared after Sarauw's method (*Annalen*, 1881, **209**, 105).   Bromine (16 g.) in 100 c.c. of ether was added to 11 g. of hydroquinone in 250 c.c. of ether, and the solution allowed to evaporate at laboratory temperature.   The residue was extracted with 250 c.c. of toluene at 90—95°, filtered off, and cooled.   Yield 10 g., m. p. 109·8°.   Recrystallised from 100 c.c. of toluene, 5 g. gave 3·8 g., m. p. 110·5°, unchanged by further recrystallisation.   Sarauw quotes m. p. 110—111°.

TABLE VII. '

−Pt | Benzoquinhydrone; $\dfrac{\text{HCl}}{0\cdot 1N}$; $\begin{array}{l}\text{Monobromohydroquinone, } 0\cdot 05M\\ \text{Benzoquinone, } 0\cdot 05M\end{array}$ Pt +

Temp.	25·4°.			18°.		18°.	
Minutes	15	30	55	80	125	15	55
Volt, I	0·0068	0·0065	0·0065	0·0065	0·0065	0·0063	0·0063₅
„ II	0·0068	0·0065	0·0065	0·0065	0·0065	0·0064	0·0064₅

$$\pi_{25°} = 0\cdot 7120. \qquad\qquad \pi_{18°} = 0\cdot 7174.$$

* After dilution with 3 vols. of 0·1*N*-HCl.

2 : 5-*Dichlorohydroquinone.*—Prepared by Ling's method (J., 1892, **61**, 558), and twice crystallised from water, the substance had a constant m. p. 169—170°.   Ling quotes 172°, and Levy and Schultz (*loc. cit.*) 166°.

TABLE VIII.

−Pt | Benzoquinhydrone; $\dfrac{\text{HCl}}{0\cdot 1N}$; $\begin{array}{l}\text{Dichlorohydroquinone, } 0\cdot 0025M\\ \text{Benzoquinone, } 0\cdot 0025M\end{array}$ Pt +

Temp.	25·4°.		18°.		18°.*
Minutes	15	30	90	150	
Volt, I	0·0121	0·0120	0·0118	0·0118	0·0117
„ II	0·0120	0·0120	0·0118	0·0118	0·0117

$$\pi_{25°} = 0\cdot 7230. \qquad\qquad \pi_{18°} = 0\cdot 7280.$$

* After dilution with 3 vols. of 0·1*N*-HCl.

2 : 5-*Dibromohydroquinone.*—Prepared by the method of Benedict (*Monatsh.*, 1880, **1**, 345) and of Sarauw (*loc. cit.*), and twice crystal-

lised from water, the compound had the m. p., 186°, recorded by those investigators.

TABLE IX.

—Pt Benzohydroquinone; $\frac{HCl}{0.1N}$; Dibromohydroquinone, $0.001M$ Pt+ Benzoquinone, $0.001M$

Temp.	25·4°.		18°.	
Minutes	30	60	90	120
Volt, I	0·0119	0·0119	0·0119	0·0119
„ II	0·0119	0·0119	0·0117	0·0117
	$\pi_{25°} = 0.7228.$		$\pi_{18°} = 0.7280.$	

Monochlorotoluhydroquinone.—Prepared by Schniter's method (*Ber.*, 1887, **20**, 2282), and crystallised from toluene and then twice from chloroform, the product had. m. p. 172—174° (uncorr.). Schniter quotes m. p. 175° [0·2048 reduced 26·0 c.c. of $0.1002N$-iodine, corresponding to 100·8% of $C_6H_2MeCl(OH)_2$. Cl, found = 22·26; calc. = 22·26%].

The hydrochloric acid used in the measurements was aerated with carbon dioxide.

TABLE X.

—Pt | Chlorotoluhydroquinone, $0.0005M$; $\frac{HCl}{0.1N}$; Benzoquinhydrone | Pt+ Benzoquinone, $0.0005M$

25°.

Temp. Minutes	10	40	100	150	175	1380
Volt, I	0·0217	0·0220	0·0222	0·0222	0·0223	0·0225
„ II	0·0214	0·0219	0·0223	0·0226	0·0227	0·0229
	Mean = 0·0224 :		$\pi_{25°} = 0.6542.$			

Dichlorotoluquinhydrone.—Prepared by oxidising the corresponding hydroquinone in 50% alcohol with the calculated quantity of ferric ammonium alum.

TABLE XI.

—Pt | Dichlorotoluquinhydrone; $0.1N$-HCl; Benzoquinhydrone | Pt +

25°.

Temp. Minutes	30	60	100	128	175	210	1110	1225
Volt, I	0·0394	0·0400	0·0406	0·0410	0·0415	0·0418	0·0425	0·0424
„ II	0·0382	0·0397	0·0400	0·0404	0·0407	0·0410	0·0424	0·0424
„ III	0·0382	0·0399	0·0400	0·0404	0·0408	0·0410	0·0424	0·0423
			$\pi_{25°} = 0.6566.$					

TABLE XII.

—Pt | Dichlorotoluquinhydrone, $0.0005M$; $0.1N$-HCl ; Benzoquinhydrone | Pt+

18°.

Temp. Minutes	20	30	45
Volt, I	0·0419	0·0419	0·0419
„ II	0·0419	0·0419	0·0419
„ III	0·0419	0·0419	0·0419
		$\pi_{18°} = 0.6625.$	

Monobromotoluhydroquinone.—To 5 g. of toluhydroquinone in 100 c.c. of ether and 45 c.c. of chloroform were added 6·45 g. of bromine in 82 c.c. of chloroform. The product (6·4 g.), recrystallised twice from toluene, melted at 176—178°. Clark (*Amer. Chem. J.*, 1892, **14**, 569) quotes 176—179°.

TABLE XIII.

$-$Pt$\begin{vmatrix}\text{Monobromotoluhydroquinone, } 0\cdot0025M \\ \text{Benzoquinone, } 0\cdot0025M\end{vmatrix}$; $\dfrac{\text{HCl}}{0\cdot1N}$; Benzoquinhydrone$|Pt+$

25°.

Temp. Minutes	15	70	185	235	510
Volt, I	0·0209	0·0210	0·0212	0·0213	0·0214
„ II	0·0205	0·0206	0·0208	0·0208	0·0212

$\pi_{25°} = 0\cdot6564.$

Dibromotoluquinhydrone.—Prepared by oxidising 1 g. of monobromotoluhydroquinone in 5 c.c. of alcohol with 12·25 c.c. of 0·2M-ferric ammonium alum, the product was washed with water and dried between filter-paper (0·2003, titrated in presence of sodium bicarbonate with 0·0849N-iodine, required 11·75 c.c. Monobromotoluhydroquinone = 50·3%; calc. 50·0%).

TABLE XIV.

$-$Pt$|$Dibromotoluquinhydrone, $0\cdot00125M$; HCl $0\cdot1N$; Benzoquinhydrone$|$Pt$+$

25·2°.

Temp. Minutes	30	90	120	155
Volt, I	0·0397	0·0399	0·0399	0·0399
„ II	0·0397	0·0399	0·0399	0·0399

$\pi_{25°} = 0\cdot6591.$

Monochloroxylohydroquinone.—Prepared by the method of v. Rad (*Annalen*, 1869, **151**, 166) and Carstanjen (*J. pr. Chem.*, 1881, **23**, 430). 20 G. of *p*-xyloquinone were added to 200 c.c. of cold concentrated hydrochloric acid, a further 300 c.c. of acid were added, and the mixture was heated for 2—3 hours on the steambath. The crystals obtained on cooling were recrystallised from toluene, carbon tetrachloride, and twice from chloroform. Yield 7·75 g., m. p. 152—153° (Cl, found 20·81, calc., 20·56%).

TABLE XV.

$-$Pt$\begin{vmatrix}\text{Monochloroxylohydroquinone, } 0\cdot002M \\ \text{Xyloquinone, } 0\cdot002M\end{vmatrix}$; $\dfrac{\text{HCl}}{0\cdot1N}$; Benzoquinhydrone$|Pt+$

25·4°.

Temp. Minutes	20	60	120
Volt, I	0·1069	0·1070	0·1069
„ II	0·1070	0·1069	0·1069

$\pi_{25°} = 0\cdot5949.$

Dichloroxyloquinhydrone.—1 G. of monochloroxylohydroquinone in 20 c.c. of water and 20 c.c. of alcohol was oxidised with 29 c.c. of $0.2N$-ferric ammonium alum. The product was washed with water. Yield 0·7 g. (0·0993 reduced 5·85 c.c. of 0·0983 N-iodine. Monochlorohydroquinone found = 49·6, calc. = 50·0%).

<div align="center">

TABLE XVI.

</div>

—Pt | Dichloroxyloquinhydrone; $0.1N$-HCl; Benzoquinhydrone | Pt +
<div align="center">25·14°.</div>

Temp.				
Minutes	30	65	125	150
Volt, I	0·1069	0·1070	0·1071	0·1071
„ II	0·1072	0·1073	0·1074	0·1074

<div align="center">$\pi_{25°} = 0.5918.$</div>

The values of π given in Tables IV, V, XI, XII, XIV, and XVI are the results of direct determinations, whilst those given in the other tables (excluding I) are indirect values.

THE UNIVERSITY, COPENHAGEN.   [*Received, August 23rd, 1924.*]

XXXIII.—*Hydrolysis of the* d-*Glucosides of* d- *and* l-*Borneol with Emulsin.*

<div align="center">By STOTHERD MITCHELL.</div>

DAKIN (*J. Physiol.*, 1904, **30**, 253) found that when an optically inactive mixture of the two methyl mandelates was acted upon by the enzyme lipase the dextro-component was hydrolysed more rapidly than the lævo. Substitution of other alkyl groups for methyl produced differences in the relative rates of hydrolysis, and in order to investigate the effect of optically active groups he prepared *l*-menthyl mandelate and *d*-bornyl mandelate. Lipase, however, was without action on these compounds. Later (*ibid.*, 1905, **32**, 199), he succeeded in hydrolysing esters in which an asymmetric carbon atom was present in the alkyl group but not in the acid part of the molecule.

The hydrolysing action of emulsin on the *d*-glucosides prepared from the two forms of borneol has now been examined.

The *d*-borneol was obtained from commercial " borneol," which is a mixture of *d*-borneol and *l-iso*borneol resulting from the reduction of camphor (Pickard and Littlebury, J., 1907, **91**, 1977). The purified *d*-borneol and the *l*-borneol used had $[\alpha]_{\text{Hg green}}^{20°} = + 42.14°$ and $- 42.20°$, respectively, calculated from 15·4% solutions in alcohol.

The β-glucosides of *d*- and *l*-borneol were prepared by treating β-tetra-acetylbromoglucose in ether with an excess of borneol in

presence of silver carbonate, the acetyl groups being subsequently removed by means of barium hydroxide (Fischer and Raske, *Ber.*, 1909, **42**, 1473; Fischer, *Ber.*, 1916, **49**, 584; Hämäläinen, *Biochem. Z.*, 1913, **50**, 217).

Emulsin (2·5 g.) was mixed with 180 c.c. of water and kept in a thermostat at 37° for a day. The solution was filtered before use and gave $\alpha_{Hg\ green}^{20°}$ — 0·64° ($l = 1$ dcm.).

A small quantity (0·3 g.) of each glucoside (which contains $1H_2O$) was placed in a 50 c.c. flask in a thermostat at 37°. The hydrolysis of the *d*-bornyl-*d*-glucoside was started by filling the flask to the mark with the emulsin solution, and an hour later the hydrolysis of the *l*-bornyl-*d*-glucoside was commenced. Two c.c. were removed at intervals and the amount of glucose present was determined by MacLean's method for estimating the sugar in blood (*Biochem. J.*, 1919, **13**, 135). The reaction constants are calculated from the usual formula for unimolecular reactions, $k = \{2 \cdot 30/(t_y - t_x)\} \log (c_x/c_y)$.

d-*Bornyl*-d-*glucoside.*				l-*Bornyl*-d-*glucoside.*			
Time in mins.	Glucose. Mg. in 2 c.c.	Glucose. Mg. in 2 c.c.	$k \times 10^5$.	Time in mins.	Glucose. Mg. in 2 c.c.	Glucose. Mg. in 2 c.c.	$\times 10^5$.
270	0·70	10·13	10	180	0·87	9·83	34
330	0·77	10·01	9	303	1·12	9·39	33
515	0·82	9·92	11	361	1·22	9·22	33
613	0·89	9·80	10	435	1·33	9·03	35
860	1·03	9·55		673	1·74	8·31	
($= t_y$)		Average 10		($= t_y$)		Averaǧ	

Hence emulsin hydrolyses *l*-bornyl-*d*-glucoside 3·4 ti: as rapidly as *d*-bornyl-*d*-glucoside. This is a striking example of the selective nature of enzyme action.

PHYSICAL CHEMISTRY DEPARTMENT,
UNIVERSITY OF GLASGOW. [*Received, November 24th, 1924.*]

XXXIV.—*Some Co-ordinated Compounds of the Alkali Metals.*

By NEVIL VINCENT SIDGWICK and SYDNEY GLENN PRESTON PLANT.

THE action of alkalis on ψ-indoxyl*spirocyclo*pentane (I) (Perkin and Plant, J., 1923, **123**, 676) has been examined and compounds of the type MB,HB [HB = (I); M = Li, Na, or K] obtained, which are soluble in toluene and behave as 4-covalent metallic compounds.
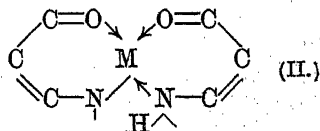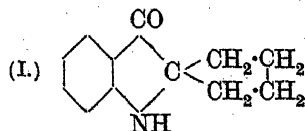
The Sodium Derivative.—Four grams of (I) were heated with sodium hydroxide (10 g.) in water (40 g.) in an air-tight steel tube at 210° for ½ hour. After cooling, the solid sodium derivative was washed out from the tube with aqueous sodium hydroxide (20%) and removed by filtration through asbestos. After drying on the steam-bath, it crystallised slowly from toluene in clusters of small, colourless prisms, melting at 204° to a cloudy liquid (Found : Na = 6·1. $C_{12}H_{12}ONNa,C_{12}H_{13}ON$ requires Na = 5·8%).

It is decomposed at once by water to re-form the indoxyl compound (I). When distilled in a vacuum, it gives a colourless distillate identical with (I); an infusible residue remains which yields (I) with dilute hydrochloric acid. Prolonged boiling with toluene causes a similar decomposition, with the separation of a colourless precipitate.

The Potassium Derivative.—Four grams of (I) were heated with 40 c.c. of aqueous potassium hydroxide (30%) in the steel tube for ½ hour at 200—210°. On pouring out, after cooling, the potassium compound appeared as an oil which soon solidified to a colourless mass. This separated from toluene in colourless plates melting to a cloudy liquid at 80—90° (Found : K = 9·6. $C_{12}H_{12}ONK,C_{12}H_{13}ON$ requires K = 9·5%). It gives (I) at once with water, and also on distillation, when it leaves an infusible residue; when it is boiled for a few minutes with toluene, a colourless precipitate separates.

The Lithium Derivative.—Four grams of (I) were heated with 40 c.c. of water saturated with lithium hydroxide at 15° for ½ hour in the steel tube at 200°. The product was washed out with lithium hydroxide solution, and removed by filtration through asbestos. After drying in a desiccator, it melted at 170° to a cloudy liquid [(I) melts at 113°] (Found : Li = 1·97. $C_{12}H_{12}ONLi,C_{12}H_{13}ON$ requires Li = 1·84%). It was decomposed by water to give the indoxyl compound. Attempts to recrystallise it from dry benzene, toluene, ligroin, and chloroform caused complete decomposition into this compound and a very small residue containing lithium.

Discussion of Results.

The action of alkali hydroxides, even in very large excess, on this indoxyl compound gives a substance MB,HB in which one metallic atom replaces one hydrogen atom in 2 mols. This loses 1 mol. of HB on heating, either alone or in toluene solution, forming, no doubt, the simple salt MB, which we should expect the indoxyl derivative to produce. There can be little doubt that the first product, MB,HB, contains a co-valent metallic atom. The indoxyl ring admits of co-ordination between a metal replacing the imide hydrogen and the carbonyl oxygen,

with the formation of the typical chelate ring of 6 atoms with two conjugate double links (see formula II), as in acetoacetic ester, acetylacetone, nitroso-β-naphthol, etc. (see Sidgwick, *Trans. Faraday Soc.*, 1923, **19**, 474). The strong tendency of the alkali metals to ionise will prevent the formation of this ring in the simple derivatives MB, which therefore are salts; but the greater stability secured by the completion of four non-polar links causes these compounds to add a second molecule of the indoxyl derivative (without replacement of hydrogen), giving the structure II.

The remarkable solubility in toluene is thus explained, since the compound is not a salt. The sodium has its octet completed by means of three pairs of shared electrons borrowed from the two oxygens and the now quadrivalent nitrogen. The second ring, being attached only by co-ordinate links, is easily removed, and hence the compound dissociates on heating.

The potassium compound is precisely similar in behaviour, although it has a markedly lower melting point (80—90° instead of 204°). Lithium seems to form an analogous compound, m. p. 170°, but owing to its great instability this could not be purified.

These appear to be the first recognised co-ordination compounds of sodium and potassium.

THE DYSON PERRINS LABORATORY,
                   OXFORD.   [*Received, November 28th*, 1924.]

XXXV.—*Reduction of the Carbocyanines.*

By FRANCES MARY HAMER.

THE constitution (I) of carbocyanine was deduced from general considerations, supported by analytical evidence, and established by the study of the oxidative breakdown of pinacyanole (Mills and Hamer, J., 1920, **117**, 1550). The prediction of similar classes of dyes, with the nuclei linked in the 4 : 4'- and 2 : 4'-positions, respectively, has now been fulfilled (Mills and Braunholtz, J.,
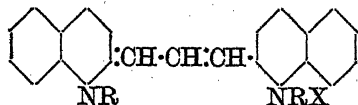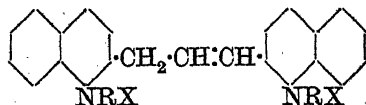
1923, **123**, 2804; Mills and Odams, J., 1924, **125**, 1913), thus confirming the formula.

Two syntheses have been adduced in its support. König's (*Ber.*, 1922, **55**, 3293) consists in condensation of quinaldine alkyl-

halide with orthoformic ester in presence of acetic anhydride. It is not obvious why this is considered to throw more light on the constitution of carbocyanine than does the earlier preparation by the action of formaldehyde on an alcoholic solution of quinaldine alkylhalide in presence of alkali (Mills and Hamer, *loc. cit.*). The synthesis by means of orthoformic ester does, however, differ from the latter, as from the preparation in which the formaldehyde is replaced by a trihalogenmethane (D.R.-P. 200,207), in that a 50% yield of analytically pure product is claimed. But when König's procedure was repeated, it was found that even twice the quoted amount of acetic anhydride was barely sufficient for solution of the given quantity of quinaldine ethiodide, and that the considerable yield of crude product consisted chiefly of impurities. The method is said to be equally applicable to the more soluble methiodide, but when this was used in order that the directions might be followed exactly, the yield of pure carbocyanine was not more than 10%. In the second synthesis (Hamer, J., 1923, **123**, 246), methylenediquinaldine dialkylhalide was prepared from quinaldine alkylhalide and formaldehyde according to the equation :
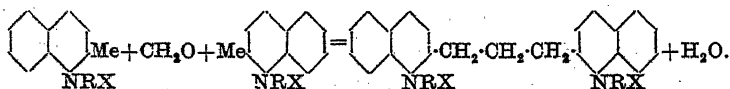
The action of alkali, in presence of quinoline alkylhalide, eliminated halogen acid with, apparently, simultaneous removal of two hydrogen atoms, since carbocyanine (I) was directly formed. This synthesis proves the existence of a three-carbon chain joining the quinoline nuclei of the carbocyanine molecule, and is unequivocal except for the unexplained fact that the presence of quinoline alkylhalide is necessary.

The converse transformation of carbocyanine into methylenediquinaldine dialkylhalide has now been accomplished, thus clearly demonstrating the relationship. The addition of hydriodic acid (b. p. 126°) to 1 : 1'-dimethylcarbocyanine iodide gave yellow crystals, too unstable to isolate for analysis, but doubtless possessing formula II, which only requires addition of two hydrogen atoms to represent methylenediquinaldine dimethiodide.

This reduction was brought about by heating with excess of hydriodic acid at a carefully regulated temperature, and a 78% yield of methylenediquinaldine dimethiodide was the result. Similarly, 1 : 1'-diethylcarbocyanine iodide and 6 : 6'-dimethyl-1 : 1'-diethylcarbocyanine iodide were reduced to methylenediquinaldine diethiodide and 6 : 6'-dimethylmethylenediquinaldine diethiodide, respectively. The temperature is an important factor in the

reduction, since with a lowering of a few degrees, unchanged carbocyanine remains, whilst too high temperatures lead to decomposition of the dialkylhalide.

p-Dimethylaminobenzylidenequinaldine ethiodide was similarly heated with hydriodic acid, but analysis of the product proved that, besides reduction of the ethylenic linking, the two methyl groups had been replaced by hydrogen atoms. That the compound was *p*-aminobenzylquinaldine ethiodide, and not the hydriodide of *p*-dimethylaminobenzylidenequinaldine, was established by the fact that it was neutral and unattacked by ammonia.

EXPERIMENTAL.

Preparation of 1 : 1′-*Dimethylcarbocyanine Iodide by Use of Orthoformic Ester* (compare König, *loc. cit.*).—Quinaldine methiodide (6 g.) was boiled with acetic anhydride (60 c.c., b. p. 135—140°), and during 5 minutes orthoformic ester (2·1 g., b. p. 142—146°) was added. The mixture was concentrated to half volume and the solid removed when cold. The greater part of the impurity was extracted by boiling methyl alcohol (15 c.c.), and the undissolved crude carbocyanine was recrystallised from methyl alcohol (yield 6% instead of 50). The method recommended in a later paper (*Ber.*, 1924, **57**, 685) gave a 10% yield.

Reduction of 1 : 1′-*Dimethylcarbocyanine Iodide.*—By heating the carbocyanine (1·5 g.) with hydriodic acid (10 c.c., b. p. 126°) in a sealed tube at 182—185° for 6 hours, black crystals of periodide were produced; addition of water gave a yellow precipitate. The total solid was suspended in boiling 1·5% hydrochloric acid, and sulphur dioxide passed in until a clear solution was obtained, when potassium iodide was added (1·5 g.). The product (yield 78%) was recrystallised from dilute hydrochloric acid, with charcoal treatment and addition of potassium iodide. The crystals were ground with pyridine (5 c.c.) to remove any acid impurity (see below), washed with acetone, recrystallised from absolute alcohol, and dried in the steam-oven (Found : C = 47·27 ; H = 4·19 ; I = 43·41. Calc. for $C_{23}H_{24}N_2I_2$, C = 47·42 ; H = 4·16 ; I = 43·61%); m. p. 207° (decomp.), alone or mixed with methylenediquinaldine dimethiodide. The compound had the properties of this substance and its crystallisation could be started by inoculation with it.

By reduction of the carbocyanine at 203—209°, the iodide obtained after two recrystallisations from absolute alcohol was strongly acid; it appeared to be free from methylenediquinaldine dimethiodide, since it was completely and easily soluble in cold pyridine, in which the dimethiodide is practically insoluble.

Reduction of 1 : 1'-*Diethylcarbocyanine Halide.*—The iodide or bromide (1 g.) was heated with hydriodic acid (7 c.c.) at 178—181° and on reduction of the resultant periodide, the crystalline product (yield 76%) was almost pure (Found : I = 41·27%). It was treated with pyridine and recrystallised from absolute alcohol (yield 54%). This reduction product, methylenediquinaldine diethiodide, and their mixture, melted simultaneously at 205° (decomp.). For analysis, it was dried in the steam-oven (Found : C = 48·80; H = 4·73; I = 41·62. Calc. for $C_{25}H_{28}N_2I_2$, C = 49·18; H = 4·63; I = 41·61%).

Reduction of 6 : 6'-*Dimethyl-*1 : 1'-*diethylcarbocyanine Iodide.*— Hydriodic acid (5 c.c.) and the carbocyanine (0·5 g.) [fine needles of the almost colourless hydriodide formed] were heated at 178—185° for 5 hours and the solid was treated with sulphur dioxide as in other cases (yield 83%). For analysis, the iodide was dried over sulphuric acid and soda-lime (Found : I = 38·97. Calc. for $C_{27}H_{32}N_2I_2,H_2O$, I = 38·68%). It melted at 219°, alone or mixed with 6 : 6'-dimethylmethylenediquinaldine diethiodide. The m. p. was unaltered by recrystallisation.

Reduction of p-*Dimethylaminobenzylidenequinaldine Ethiodide.*— This was prepared by the method of König and Treichel (*J. pr. Chem.*, 1921, [ii], **102**, 63). By increasing the time of heating from 1 hour to 24 hours, the yield of recrystallised product was raised from 23 to 76% (Found : I = 29·33; calc. 29·51%); m. p. 259—263° (decomp.).

p-Dimethylaminobenzylidenequinaldine ethiodide (1·5 g.) and hydriodic acid (10 c.c.) were heated for 3 hours at 178—181°, water was added, and the solid, in boiling dilute hydrochloric acid, treated with sulphur dioxide. The clear solution gave no precipitate with potassium iodide (1·5 g.), but ammonia produced an orange tar which hardened, and was powdered, filtered, and dried in a vacuum desiccator. From absolute alcohol, it separated as clear red crystals (yield 59%). A thrice recrystallised specimen was dried in a vacuum desiccator and was shown by analysis to be p-aminobenzylquinaldine ethiodide (Found : C = 56·64; H = 5·26; N = 7·08; I = 31·30. $C_{19}H_{21}N_2I$ requires C = 56·41; H = 5·24; N = 6·93; I = 31·41%). It is moderately soluble in alcohol or water; m. p. 200—201°, with incipient softening a couple of degrees lower.

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XXXVI.—*Fission of the Pyridine Nucleus during Reduction. Part II. The Preparation of Glutardialdoxime.*

By BRIAN DUNCAN SHAW.

THE suggestion (J., 1924, **125**, 3041) that the initial product of the action of sodium and alcohol on pyridine is 1 : 4-dihydropyridine has now been confirmed, for, although this has not been isolated, if the solution is treated with hydroxylamine, ammonia is evolved, and a good yield (70%) of glutaraldehydedioxime obtained. This value is obviously too low, since some of the dihydro-compound is further reduced. The initial reduction product, therefore, is largely, if not entirely, 1 : 4-dihydropyridine.

Further work on glutardialdehyde and its homologues is in progress.

EXPERIMENTAL.

Pyridine, b. p. 115—116°, was heated at 80° with 4% potassium permanganate solution until a pink colour persisted. The purified base was separated by distillation, dried over caustic soda, and boiled with powdered calcium carbide. The alcohol was boiled with powdered calcium carbide and fractionated through a column filled with freshly-broken lumps of the same material.

Glutardialdoxime.—No ammonia was evolved when pyridine (80 g.) in boiling alcohol (400 c.c.) was treated with sodium (24 g.). Hydroxylamine hydrochloride (36 g.) in dry alcohol was added, and the mixture boiled for a few minutes, when ammonia was evolved copiously. The remainder of the sodium was precipitated by addition of the requisite quantity of hydrochloric acid diluted with alcohol. After 2 hours' boiling, the sodium chloride was removed and the filtrate distilled until only 80 c.c. remained. The oxime separated slowly and a further quantity was obtained from the mother-liquor (yield 28 g. or 65% calculated on the hydroxylamine); m. p. 175° after recrystallisation from water or pyridine. It may be sublimed without decomposition. Its identity was established by analysis (Found : N = 21·2; calc. 21·05%), by its reactions, and by reduction to pentamethylenediamine (some piperidine was also produced). Boiling with hydrochloric acid gave pyridine (compare Braun and Danziger, *Ber.*, 1913, **46**, 103). When amyl alcohol was used for the reduction, little hydrogen was evolved, and the yield, calculated on the assumption that the sodium liberated the theoretical quantity of hydrogen and that only 1 : 4-dihydropyridine was produced, varied from 68—72%. Excess of hydroxylamine was used in these cases.

Glutardialdehyde was obtained from the oxime by the method used by Harries in the case of succindialdehyde. Both the glass-like polymeride and the unimolecular form described by Harries and Tank (*Ber.*, 1908, **41**, 1705) were obtained.

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XXXVII.—*The Action of Bromine on Sodium and Silver Azides.*

By DOUGLAS ARTHUR SPENCER.

Part I. Bromoazoimide.

DURING the course of experiments, suggested by Professor H. B. Baker, aiming at the preparation of triatomic nitrogen, bromine vapour, diluted with nitrogen, was passed over sodium azide. The colour of the gaseous mixture faded considerably, but was not completely discharged however long the bromine remained in contact with the azide, and the gas leaving the apparatus had a pungent but sickly smell reminiscent of hydrazoic acid and dilute bromine vapour.

An aqueous solution of the gas was yellow, gave a blood-red coloration with ferric chloride, smelled of hypobromous and hydrazoic acids, and slowly evolved nitrogen on standing.

Preliminary attempts to freeze out any compound formed resulted in violent explosions which occasionally detonated the sodium azide. The dilute gas mixture is itself extremely sensitive to shock or rise of temperature, the explosion being accompanied by a flash of livid blue light whilst the glass parts of the apparatus are reduced to powder.

The analysis was therefore performed indirectly as follows : Pure carbon dioxide, generated by the action of boiled-out hydrochloric acid on calcite, was washed with sodium bicarbonate and dried by sulphuric acid and phosphorus pentoxide, and was used to carry bromine vapour (derived from the liquid at 5°) over a large surface of sodium azide, contained in a glass tube 175 cm. long and 0·5 cm. in diameter, coiled into a spiral and kept at 0°.

The gas current was adjusted to carry about 0·05 g. of bromine over the azide per hour. The pale yellow gas so obtained was passed through a hard glass tube, 10 cm. long, packed with glass fragments and heated at the far end by a small bunsen flame. By this means, the compound was decomposed without explosion and the gas acquired the much darker red colour characteristic of bromine vapour. The products of decomposition were passed over silver leaf into a potash nitrometer, the carbon dioxide stream being stopped when the volume of gas in the latter had remained constant for ½ hour. The volume of this gas, which was pure nitrogen having the normal density, was measured over water and reduced to that at $N.T.P.$ The excess of silver leaf was dissolved in nitric acid and the silver bromide determined gravimetrically. The results are tabulated below.

TABLE I.

Expt. No.	Duration in hours.	Bromine taken (g.).	Bromine recovered (g.).	C.c. of N_2 obtained.	$N_3 : Br_x$. x.
1	2	0·1684	0·1247	37·07	1·41
2	5½	0·3938	·0·2128	74·10	1·26
3	2½	—	0·1549	57·60	1·13
4	4½	0·1935	0·09447	36·00	1·11
5	6½	0·1701	0·0802	28·80	1·14
6	9½	0·2906	0·1324	50·00	1·13
7	10½	0·3833	0·1706	61·65	1·15

Excluding the results of experiments 1 and 2, in which the bromine vapour was in contact with the azide for a comparatively short period, the mean value is $N_3 : Br_{1·13}$.

Whilst pointing to the presence of *bromoazoimide*, N_3Br, the analyses show that there is about 8% more bromine in the gas than is required by the simple formula. Since the quantity of bromine recovered agrees with that required by the equation $NaN_3 + Br_2 = NaBr + N_3Br$, it was at first thought that this excess was due to a deficiency in the volume of nitrogen obtained, but the density, viscosity and chemical behaviour of the nitrogen were normal and therefore it is improbable that any polymeric modification was present, even if it could have survived the heating. A second possibility was that the reaction was reversible or incomplete, but alterations in the temperature of the reaction tube, and of the time of contact of the bromine with the sodium azide, did not materially affect the final analysis. The formation of some other nitrogen bromide, *e.g.*, NBr_3, was a third possibility.

By using a fine capillary tube as connecting link between the reaction tube and condensing vessels, any explosion could be localised, and, by immersing these vessels in freezing mixtures kept in unsilvered Dewar flasks standing in large beakers of water, rendered less dangerous. It then became possible to freeze the substance

out, and to fractionate it by passing a stream of nitrogen over the surface whilst allowing the temperature to rise.

The analysis of these fractions was carried out as follows : The vapour derived from each fraction was absorbed in standardised solutions of carbonate-free caustic soda containing hydrogen peroxide. With this mixture the compound forms sodium azide and sodium bromide, the hydrogen peroxide reducing the sodium hypobromite first formed :

$$N_3Br + 2NaOH = NaBrO + NaN_3 + H_2O.$$
$$NaBrO + H_2O_2 = NaBr + H_2O + O_2.$$
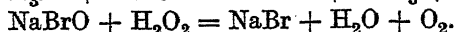
By titrating the excess of sodium hydroxide with $N/10$-sulphuric acid and phenolphthalein, the amount of alkali required to combine with the N_3 and Br radicals was found. A known excess of silver nitrate was then added, silver bromide and azide being precipitated. The mixture was boiled with nitric acid until all the silver azide had been decomposed and the hydrazoic acid driven off. The cooled solution was titrated with ammonium thiocyanate, giving a measure of the silver nitrate required to precipitate the bromide present.*

The results are summarised in Table II.

TABLE II.

Expt.	Fraction.	a.	b.	t.	$N_3 : Br_3$. x.
1	1st	91·80	48·30	−10°	1·06
	2nd	84·70	43·70	+ 5	1·07
2	1st	117·9	58·06	−18	0·97
	2nd	58·55	32·71	+ 5	1·26
3	1st	29·04	14·73	−20	1·036
	2nd	52·17	27·19	−10	1·09
	3rd	90·51	50·67	+ 5	1·18

a = c.c. of $N/10$-NaOH neutralised = N_3 + Br; b = c.c. of $N/10$-AgNO$_3$ required to neutralise Br; t = temperature below

* The above procedure provides a method for the estimation of soluble azides in presence of halides which has decided advantages over the gravimetric determination (Dennis and Isham, J. Amer. Chem. Soc., 1907, 29, 18). Owing to the number of operations involved, and the appreciable solubility of silver azide at normal temperatures, the latter method is tedious and liable to error, the results being usually low. On the other hand, the volumetric method—titration with silver nitrate followed by treatment with nitric acid and thiocyanate—is both rapid and trustworthy if the solution is first rendered barely acid by the addition of sodium acetate and acetic acid. If potassium arsenate is used as indicator in the first titration, the final acid solution is colourless. The colour of silver arsenate is, however, not so intense as that of the chromate, and quite accurate results may be obtained with the latter. Owing to the solution being slightly acid with acetic acid, a small amount of dichromate is formed and the solution is of a yellow-orange colour rather than the usual bright yellow, and the use of a comparison basin is advisable.

which the fraction was obtained.   C.c. of $N/10$-NaOH equivalent to $N_3 = a - b$.

The first fractions (with a mean value of $N_3 : Br_{1\cdot02}$) were dark orange-red liquids which solidified at about $-45°$ to dark red solids. The later fractions were ruby red, but even these were distinctly lighter and apparently much more mobile than liquid bromine.

If the high bromine content is due to the presence of free bromine, it should be possible to remove this by treating the liquid with sodium azide.   A first fraction, obtained at $-15°$, was distilled on to sodium azide kept at $-25°$.   The colour of the liquid was not altered, even after 3 hours' contact (Found : $N_3 : Br_{1\cdot04}$).   Also when gas derived directly from the apparatus and of approximate composition $N_3Br_{1\cdot13}$ (see Table I) was condensed on to sodium azide, and, after 3 hours, the liquid was allowed to vaporise, the proportions were $N_3 : Br_{1\cdot16}$.   The excess of bromine, therefore, is not present in the free state and the most probable explanation is that it is in the form of nitrogen tribromide, NBr_3.   When the gas was passed into water the solution contained, in addition to hydrazoic and hypobromous acids, traces of ammonium salts. This cannot, however, be taken as a proof of the presence of NBr_3, for Hantzsch states that iodoazoimide (triazo iodide) gives rise to a small quantity of ammonia on hydrolysis (compare L. Spiegel, " Der Stickstoff," 1903, pp. 35, 36).

Hantzsch (*Ber.*, 1900, **33**, 522), by the interaction of silver azide (but not potassium azide) and iodine in ether solution at $0°$ and evaporation of the ether, obtained red crystals of the highly unstable iodoazoimide, N_3I (which he states is probably colourless when pure).   A freshly prepared aqueous solution is neutral towards litmus and starch, but hydrolyses fairly rapidly to hydrazoic and hypoiodous acids.   In non-aqueous solvents, the compound slowly decomposes to iodine and nitrogen.

When either sodium or silver azide is treated with bromine dissolved in ether, benzene, or ligroin, bromoazoimide is formed, but the method is not a convenient one.   The bromine attacks the solvent to a certain extent and, owing to the great solubility and volatility of bromoazoimide, it is impossible to separate it from the solvent.   Moreover, the presence of traces of water results in the immediate hydrolysis of the compound to hydrazoic and hypobromous acids.   This is most striking in the case of silver azide–bromine mixtures, as the admission of a drop of water results in a vigorous evolution of nitrogen due to the rapid reaction of the hypobromous acid at once produced, with the silver azide.

Properties of Bromoazoimide.—The purest sample of the bromide obtained in these experiments was a mobile, very volatile, orange-

red liquid, which changed to a dark red solid at about −45°. The pungent vapour has toxicological properties similar to hydrazoic acid, causing giddiness, headache, and a slackening of the muscles when inhaled. Traces of the vapour irritate the eyes and cause a slight difficulty in breathing, due apparently to congestion of the nasal mucous membrane.

Solid, liquid, and vapour are as sensitive to shock as iodoazoimide, the explosion (often apparently spontaneous) being accompanied by a flash of livid blue light. Some idea of the instability of the compound, even at −200°, may be gathered from the fact that, of twenty-four attempts at freezing the compound and determining its melting point, only six were completed without explosion. Fortunately, in the majority of cases, the sphere of action was limited to a radius of about 3 feet. Within this radius, all glass apparatus was reduced to powder; beyond it, a reinforced glass screen proved a sufficient protection. The liquid explodes in contact with phosphorus, arsenic, sodium, and silver foil, but the vapour, when diluted with nitrogen and passed over silver leaf or sodium, gives a film of the corresponding azide and bromide.

The liquid is apparently miscible in all proportions with ether, but is less soluble in benzene or ligroin. These solutions are stable for a few hours in the dark, but, when concentrated, are liable to explode on shaking, and on standing gradually decompose, giving nitrogen and bromine, the latter attacking the solvent. When passed into water, bromoazoimide hydrolyses instantaneously, giving a mixture of hydrazoic and hypobromous acids, and the solution, on standing, evolves nitrogen by the interaction of these acids. When bromoazoimide is passed into potassium iodide solution, iodine is liberated equivalent to the hypobromous acid produced and potassium azide is obtained :

$$N_3Br + 2KI = KN_3 + KBr + I_2.$$

This experiment was performed by substituting a potassium iodide absorption vessel for the heated glass decomposition tube in the apparatus described on p. 216, and it is possibly significant that 6 c.c. of nitrogen collected in the nitrometer. Some of this nitrogen may have been due to a slight decomposition of the bromoazoimide into its elements before it reached the absorption vessel, but in view of the fact that no free bromine was detected when the compound was distilled on to sodium azide (p. 219), this does not seem probable. It is thought, therefore, that the nitrogen may have been derived from NBr_3 present.

Part II.

Since bromoazoimide is instantly hydrolysed by water, the reaction in aqueous solution between bromine and sodium azide should yield hydrazoic and hypobromous acids, and therefore should differ from that between iodine and sodium or potassium azide, which occurs only in presence of sulphur compounds, yielding nitrogen (Raschig, *Chem. Ztg.*, 1908, **32**, 1203; Browne, *J. Amer. Chem. Soc.*, 1922, **44**, 2106).

When sodium azide solution was added to $N/10$-bromine water, the colour of the mixture faded at once to a pale straw-yellow and nitrogen was evolved at a rate depending on the concentration, temperature, and proportions of the solutions. Approximately

FIG. 1.
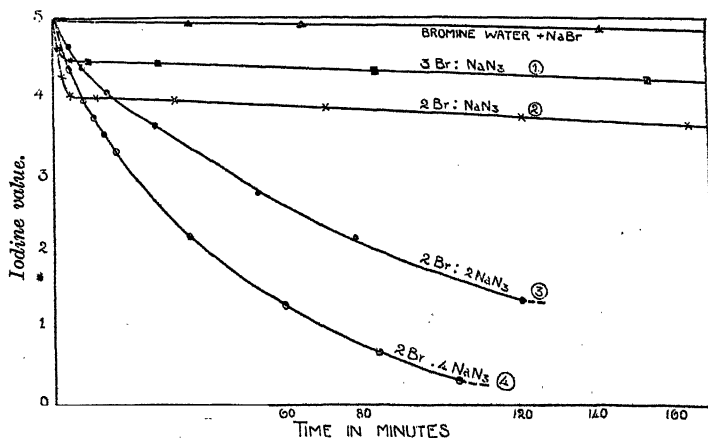
94% of the expected volume of nitrogen was evolved in 15 hours from concentrated solutions at the ordinary temperature. The gas was contaminated with oxygen, hydrazoic acid, and hypobromous acid.

The course of the reaction with various proportions and concentrations of the reactants can conveniently be followed by plotting the fall in iodine value of the solution against time.

Aliquot portions of the effervescing solution, removed at fixed intervals, were added to potassium iodide, and the iodine liberated by the hypobromous acid was titrated with $N/10$-sodium arsenite (thiosulphate is unsuitable, as it causes an instantaneous liberation of all the available nitrogen. Browne, *loc. cit.*).

In the figure, typical curves obtained with $N/10$-solutions at 15° are plotted.

Hypobromous acid reacts somewhat slowly with hydrazoic acid,

but rapidly with sodium azide solutions (the latter are always alkaline by hydrolysis, and sodium hypobromite is dissociated to a greater extent than hypobromous acid). Curves 1 and 2 correspond therefore to the slow fall in concentration of hypobromous acid with hydrazoic acid, and curves 3 and 4 to the fall in the presence of an excess of sodium azide.

An abrupt change in the slope of the curves occurs when one uses more than one equivalent of sodium azide to two of bromine.

$$NaN_3 + Br_2 + H_2O = NaBr + HN_3 + HBrO \qquad . \qquad . \quad (1)$$
$$HBrO + 2HN_3 = HBr + H_2O + 3N_2 \qquad . \qquad . \quad (2)$$
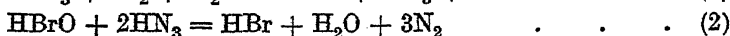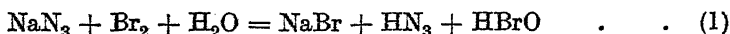
Since one equivalent of hypobromous acid can decompose two equivalents of hydrazoic acid, there is, in the solution, sufficient hypobromous acid to decompose a further equivalent of sodium azide :—

$$HBrO + 2NaN_3 = NaBr + NaOH + 3N_2 \qquad . \qquad . \quad (3)$$
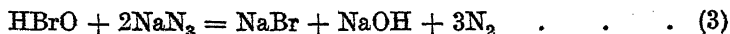
Equivalent proportions of sodium azide solution and bromine water were mixed. After 17 hours, gas evolution had ceased and the solution was colourless and exactly neutral :—

$$NaN_3 + Br_2 + H_2O = NaBr + HBrO + HN_3 \qquad . \qquad . \quad (1)$$
$$NaN_3 + HBrO + HN_3 = NaBr + H_2O + 3N_2 \qquad . \qquad . \quad (4)$$
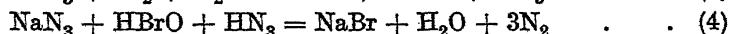
One equivalent of sodium azide was mixed with two equivalents of bromine water. The effervescence was much slower, resembling that obtained when mixtures of hydrazoic and hypobromous acids react in presence of sodium bromide.

$$NaN_3 + Br_2 + H_2O = NaBr + HBrO + HN_3 \qquad . \qquad . \quad (1)$$
$$HN_3 + \tfrac{1}{2}HBrO = \tfrac{1}{2}HBr + \tfrac{1}{2}H_2O + 1\tfrac{1}{2}N_2 \qquad . \qquad . \quad (2)$$
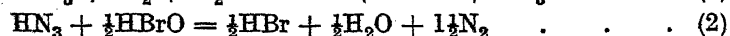
The solution should therefore contain equal parts of hydrobromic and hypobromous acids amounting to one equivalent at the conclusion of the experiment.

The nitrogen evolved would be expected to carry away the greater part of these volatile acids and yet, after 17 hours, the solution still contained a little more than a quarter of an equivalent of acid, one-half of which consisted of hypobromous acid, the other half being presumably hydrobromic acid, since there was only the slightest trace of azoimide.

The Reaction between Bromine Water and Silver Azide.—Silver azide, precipitated from a solution of sodium azide slightly acidified with nitric acid, was washed until free from soluble silver salts and treated with freshly-prepared bromine water. A vigorous

reaction took place and silver bromide was obtained (in daylight, the yellow precipitate at once commenced to turn slate-blue unless excess of bromine was present). The evolved gas contained traces of azoimide together with about 1% of oxygen, but no nitrogen oxides, and after drying with lime and phosphorus pentoxide, had the density of ordinary nitrogen.

About 92% of the nitrogen expected from the equation $2AgN_3 + Br_2 = 2AgBr + 3N_2$ was obtained within 10 minutes of the mixing, but the presence of hydrazoic acid and oxygen suggests that the side reaction $AgN_3 + Br_2 = AgBr + N_3Br$ probably occurs in a manner analogous to the formation of iodoazoimide (Hantzsch, *loc. cit.*). The bromoazoimide was instantly hydrolysed by the water, the oxygen being derived by decomposition of the hypobromous acid thus produced (compare Fleury, *Compt. rend.*, 1920, **171**, 957). The formation of hydrazoic acid in this manner accounts for the deficiency in nitrogen, as azoimide is only slowly attacked by hypobromous acid; the latter moreover reacts very rapidly with silver azide.

Summary.

In the absence of water, bromine reacts with sodium and silver azides to give the highly unstable bromoazoimide :

$$XN_3 + Br_2 = XBr + N_3Br.$$
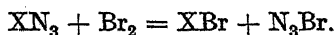
This compound (m. p. about $-45°$), whilst resembling iodoazoimide in its general properties, differs in its greater volatility and immediate decomposition by water.

Bromine water reacts instantly with sodium azide solutions to give a mixture of hydrazoic and hypobromous acids, which then interact to produce nitrogen. When the sodium azide is present in larger quantities than are required by the equation $NaN_3 + Br_2 + H_2O = NaBr + HN_3 + HBrO$, the nitrogen evolution is more rapid owing to the interaction of the hypobromous acid with the excess of sodium azide, and it is for this reason that two equivalents of bromine are able to decompose two equivalents of sodium azide.

The reaction between silver azide and bromine water differs from that with iodine solutions in that it is better represented by the equation

$$2AgN_3 + Br_2 = 2AgBr + 3N_2.$$

The only evidence for the momentary existence of bromoazoimide in aqueous solution is the formation of a certain amount of azoimide with consequent loss of free nitrogen.

The density or viscosity of all nitrogen samples was determined,

but no indication of the existence of the polymeride N_3 was obtained.

My thanks are due to Professor H. B. Baker, at whose suggestion, and under whose supervision, the work has been carried out.

XXXVIII.—*The Constitution of Disulphoxides. Part II.*

By CECIL JAMES MILLER and SAMUEL SMILES.

ALTHOUGH the symmetrical structure of the disulphoxides (I) has been generally accepted, the evidence adduced in its favour has been incorrectly interpreted and is in fact ambiguous, and many simple reactions of these substances appear clearly to indicate the thiosulphonate structure (II), such, for example, as their behaviour with zinc dust, potassium sulphide, sodium arsenite, and mercaptans (J., 1924, **125**, 176). Moreover, this view is supported by syntheses of disulphoxides from sulphenic halides and silver sulphinates (Zincke, *Annalen*, 1912, **391**, 67). Since all the definite evidence thus favoured the thiosulphonate structure, it was concluded that this should not be abandoned, but instead should be regarded as the most probable until final proof of one structure or another was forthcoming.

$$\text{(I.)} \quad \underset{\underset{O\ O}{|\ |}}{Ar\cdot S\cdot S\cdot Ar} \qquad \underset{\text{(II.)}}{Ar\cdot SO_2\cdot S\cdot Ar} \qquad \underset{\underset{O}{|}}{Ar\overset{\centerdot}{S}\cdot O\cdot SAr} \quad \text{(III.)}$$
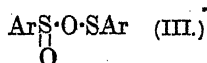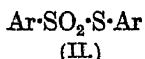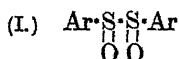
The experiments now described provide the necessary further proof of this unsymmetrical constitution, in that (1) the action of Grignard's reagent with the disulphoxides must be added to those already quoted as indicating this structure, (2) the reduction of disulphoxides with hydrogen iodide, which hitherto has been quoted as the main evidence for the symmetrical formula, is not only useless as such, but accords with the thiosulphonate structure, (3) the unsymmetrical character of the disulphoxides is demonstrated by synthesis.

Although the behaviour of numerous carbon compounds of sulphur with alkyl and aryl magnesium halides has been investigated (Lapworth, J., 1912, **101**, 297; Hepworth and Clapham, J., 1921, **119**, 1188; Wedekind, *Ber.*, 1921, **54**, 1604), that of the disulphoxides appears to have escaped attention. These substances are very readily attacked by the magnesium compounds, and, using

equimolecular proportions of the reactants, high yields of the sulphinic acids have been isolated, fission of the disulphoxide taking place apparently according to the following scheme (IV):

$$\text{(IV.)} \quad \begin{array}{c} \text{Ar·SO}_2\text{··S·Ar} \\ \text{IMg}\vdots\text{R} \end{array} \qquad\qquad \begin{array}{c} \text{Ar·SO··SO·Ar} \\ \text{IMg}\vdots\text{R} \end{array} \quad \text{(V.)}$$

The sulphinic acid was obtained in every case examined, but the fate of the thioaryl group of the disulphoxide varied according to the nature of the magnesium compound used : with magnesium methyl iodide, the methyl aryl sulphide, Ar·S·CH_3, was commonly obtained, whilst with magnesium phenyl iodide the disulphide and diphenyl also were observed. The chief point at issue is the situation of the oxygen in the molecule of the disulphoxide, and with the symmetrical formula it is very difficult to explain the isolation of 80% of this as sulphinic acid. According to this symmetrical constitution, it would be expected that fission of the molecule would result in the formation of a sulphoxide (V), but this has not been observed. The results of this decomposition evidently support the unsymmetrical structure and appear inexplicable on the basis of the symmetrical formula. The mode of experiment is described and the results are tabulated on subsequent pages.

The fact that the disulphoxides are easily reduced by hydrogen iodide to disulphides has been regarded as sufficient reason for rejecting the thiosulphonate structure and as proving the presence of the true disulphoxide arrangement (Hinsberg, *Ber.*, 1908, **41**, 2836, 4294; 1909, **42**, 1278; Fries, *Ber.*, 1914, **47**, 1195). It is assumed that the reduction is direct, and since the sulphonyl group usually is not easily reduced by this reagent whilst the thionyl group is readily attacked, the conclusion would seem justified, but it has been pointed out (Smiles and Gibson, J., 1924, **125**, 176) that the force of the argument depends on the assumption that reduction is direct and is not accompanied by fission of the molecule. If, however, rupture does take place, the reduction cannot be used as an argument against the unsymmetrical or in favour of the symmetrical formula, for in either case a disulphide must be expected as the final product of the reaction. The question whether this fission takes place or not may be answered by the reduction of a disulphoxide containing different aromatic groups. In such a case, if the unsymmetrical disulphide is the sole product (VI), the assumption of direct reduction is clearly justified, but if both, or even one, of the symmetrical disulphides are obtained (VII) it must be admitted that rupture of the dithio-system has taken place.

$$\text{(VI.)} \quad \text{R}^1\text{·SO·SO·R}^2 \longrightarrow \text{R}^1\text{·S·S·R}^2$$
$$\text{(VII.)} \quad 2\text{R}^1\text{·S}_2\text{O}_2\text{·R}^2 \longrightarrow (\text{R}^1\text{S})_2 + (\text{R}^2\text{S})_2$$

I
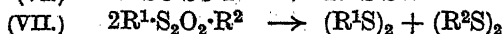
Disulphoxides containing different aromatic nuclei are readily prepared by an extension of the synthetical method of Zincke (*loc. cit.*) For example, when the silver salts of *p*-toluenesulphinic acid and *p*-chlorobenzenesulphinic acid are treated with *o*-nitrophenyl-sulphur chloride, the *o-nitrophenyl* p-*toluenethiolsulphonate* (VIII) and *o-nitrophenyl* p-*chlorobenzenethiolsulphonate* (IX) are respectively formed.

$$NO_2 \cdot C_6H_4 \cdot SCl + AgSO_2 \cdot C_7H_7 = AgCl + NO_2 \cdot C_6H_4 \cdot S \cdot SO_2 \cdot C_7H_7.$$
$$\text{(VIII.)}$$

$$NO_2 \cdot C_6H_4 \cdot SCl + AgSO_2 \cdot C_6H_4Cl = AgCl + NO_2 \cdot C_6H_4 \cdot S \cdot SO_2 \cdot C_6H_4Cl$$
$$\text{(IX.)}$$
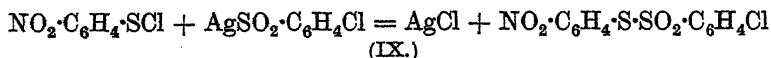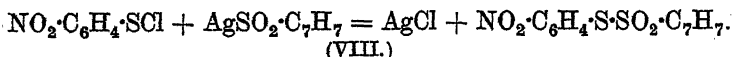
Reduction of these substances with hydrogen iodide in the usual manner (compare Hinsberg, *loc. cit.*) furnished *o*-nitrophenyl disulphide, $(NO_2 \cdot C_6H_4 \cdot S \cdot)_2$, in good yield and in the case of the chloroderivative *p*-chlorophenyl disulphide also was isolated. Hence it is clear that the disulphoxide system has been broken during the process of reduction and the reaction cannot be admitted as evidence favouring the symmetrical and excluding the unsymmetrical structure. Nothing else can be deduced from this result, but further information has been gained by adopting milder conditions of reduction with hydrogen iodide or by the use of dilute hyposulphite (in presence of sodium carbonate). The derivative (VIII) then yielded *p*-toluenesulphinic acid and the nitrophenyl disulphide, the chloronitro-derivative (IX) gave *p*-chlorobenzenesulphinic acid and the nitro-disulphide, whilst *p*-tolyl disulphoxide and *p*-chlorophenyl disulphoxide gave the corresponding sulphinic acids and disulphides or mercaptans. These results are similar to those obtained by Gutmann (*Ber.*, 1914, **47**, 635) on reduction with sodium arsenite. In the cases of disulphoxides containing similar aromatic groups, this result does not enable a decision to be made in favour of either structure, for both permit the formation of a sulphinic acid by hydrolytic fission,

$$R \cdot SO \cdot SO \cdot R \longrightarrow R \cdot SO_2H + R \cdot S \cdot OH \longleftarrow R \cdot SO_2 \cdot SR$$
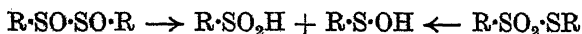
whilst the disulphide would result from reduction of the less stable sulphenic acids. Turning to the case of a disulphoxide containing different aromatic groups, a distinction between the requirements of either structure is found. On the basis of the symmetrical arrangement, the formation of two sulphinic acids may be expected, for there is no reason to suppose that hydrolysis will take place in one direction only when R^1 and R^2 are of similar character :

$$R^1S \cdot OH + R^2 \cdot SO_2H \longleftarrow R^1 \cdot SO \cdot SO \cdot R^2 \longrightarrow R^1 \cdot SO_2H + R^2 \cdot S \cdot OH.$$

On the other hand, according to the thiosulphonate structure only one sulphinic acid should be formed :

$$2R^1 \cdot SO_2 \cdot S \cdot R^2 \longrightarrow 2R^1 \cdot SO_2H + (SR^2)_2$$
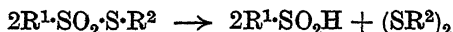
The latter condition accords with the result obtained by the reduction of these substances, only one sulphinic acid has been isolated in each case examined. Moreover, it is significant that the sulphinic acid isolated was always the one which had been used as a component in the synthesis, thus nitrophenyl toluenethiolsulphonate (VIII) yielded p-toluenesulphinic acid and o-nitrophenyl disulphide,

$$2C_7H_7 \cdot SO_2 \cdot S \cdot C_6H_4 \cdot NO_2 \longrightarrow 2C_7H_7 \cdot SO_2H + (NO_2 \cdot C_6H_4 \cdot S \cdot)_2,$$
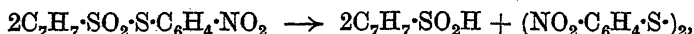
and nitrophenyl chlorobenzenethiolsulphonate (IX) gave p-chloro-benzenesulphinic acid and the nitro-disulphide :

$$2C_6H_4Cl \cdot SO_2 \cdot S \cdot C_6H_4 \cdot NO_2 \longrightarrow 2C_6H_4Cl \cdot SO_2H + (NO_2 \cdot C_6H_4 \cdot S \cdot)_2.$$
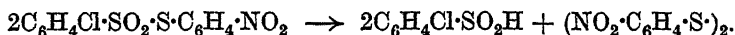
The action of mercaptans with these disulphoxides is closely analogous (compare Smiles and Gibson, *loc. cit.*). o-Nitrophenyl mercaptan yields in both cases the o-nitrophenyl disulphide and the correponding sulphinic acid :

$$C_7H_7 \cdot SO_2 \cdot S \cdot C_6H_4 \cdot NO_2 \qquad\qquad C_6H_4Cl \cdot SO_2 \cdot S \cdot C_6H_4 \cdot NO_2$$
$$H S \cdot C_6H_4 \cdot NO_2 \qquad\qquad\qquad H S \cdot C_6H_4 \cdot NO_2$$

The information gained from this extended study of the reduction of the disulphoxides therefore clearly favours the unsymmetrical structure. Taking a general review of the characteristic reactions of the disulphoxides, it is seen that all yield the sulphinic acid and a product which contains the thioaryl group; these substances result from the action of zinc dust, magnesium alkyl halides, potassium sulphide, mercaptans, and of arsenite and other mild reducing agents. The majority of these reactions indicate an unsymmetrical structure, a few are ambiguous in their import, whilst none insists on the symmetrical arrangement.

To establish more firmly the unsymmetrical constitution, disulphoxides each containing different aromatic groups have been synthesised by alternate methods. In the first series of experiments it seemed desirable to arrange that the aromatic groups R^1 and R^2 should differ by the nature of the substituents present and not merely by the position of these. The more stable of the known aromatic sulphur chlorides contain the nitro-group and it was obvious to choose one of these as a component of one method of synthesis, but the chief difficulty lay in obtaining a sulphur chloride of sufficient stability without this group for use in the alternate

process. This was overcome by the preparation of 2 : 5-dichloro-phenylsulphur chloride (X) from the corresponding disulphide and chlorine.

From 2-nitrophenylsulphur chloride and silver 2 : 5-dichloro-benzenesulphinate a *disulphoxide* (XIa) of m. p. 142° was obtained, whilst from 2 : 5-dichlorobenzenesulphur chloride and silver 2-nitro-benzenesulphinate an isomeric compound (XIIa) melting at 129° was prepared. These substances differ not only in their physical properties but also in their chemical behaviour. When 2-nitro-phenyl 2 : 5-dichlorobenzenethiolsulphonate (XIa) is treated with 2-nitrophenyl mercaptan, the dichlorobenzenesulphinic acid and *o*-nitrophenyl disulphide are formed (XI), whilst the action of the same mercaptan with 2 : 5-dichlorophenyl 2-nitrobenzenethiol-sulphonate (XIIa) yields *o*-nitrobenzenesulphinic acid and a mixture of the two possible disulphides (compare Smiles and Gibson, *loc. cit.*).

Cl
$\bigwedge$ SCl (a)C$_6$H$_3$Cl$_2$·SO$_2$·S·C$_6$H$_4$·NO$_2$ (a) C$_6$H$_3$Cl$_2$·S·SO$_2$·C$_6$H$_4$·NO$_2$
$\bigvee$ H·S·C$_6$H$_4$·NO$_2$ C$_6$H$_3$Cl$_2$·S·H
Cl (X).   (XI.)   (XII.)
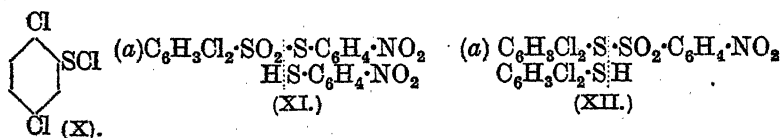
The action of 2 : 5-dichlorophenyl mercaptan with the latter di-sulphoxide yielded (XII) the nitrosulphinic acid and the tetra-chloro-disulphide. Mild reduction of these disulphoxides gave analogous results; these are collected on a subsequent page.

A second series of experiments was made with material in which the groups R^1 and R^2 were closely similar, for it was thought that such conditions would be favourable to intramolecular change—if indeed this were possible—of one thiolsulphonate to the other or of the thiolsulphonate to the true α-disulphoxide structure, the latter change having been suggested by previous workers (Hinsberg, *loc. cit.*; Fries, *loc. cit.*). The materials chosen were the 2 : 5-dichloro-and 2 : 5-dibromo-phenyl derivatives. Thus 2 : 5-dichlorophenyl-sulphur chloride (X) and silver 2 : 5-dibromobenzenesulphinate furnished 2 : 5-dichlorophenyl 2 : 5-dibromobenzenethiolsulphonate (XIIIa), which melted at 119° even after being heated to 150° and cooled.

On treatment with 2 : 5-dichlorophenyl mercaptan the tetra-chloro-disulphide and 2 : 5-dibromobenzenesulphinic acid were formed (XIII), the structure indicated by synthesis being thus confirmed.

(a) C$_6$H$_3$Cl$_2$·S·SO$_2$·C$_6$H$_3$Br$_2$ (a) C$_6$H$_3$Cl$_2$·SO$_2$·S·C$_6$H$_3$Br$_2$
C$_6$H$_3$Cl$_2$·S·H   H·S·C$_6$H$_3$Br
     (XIII.)   (XIV.)

The isomeric 2 : 5-dibromophenyl 2 : 5-dichlorobenzenethiol-sulphonate (XIVa), prepared in a similar manner, melted at 125° and with 2 : 5-dibromophenyl mercaptan yielded the tetrabromo-disulphide and 2 : 5-dichlorobenzenesulphinic acid (XIV).

In summarising the results of these experiments, it is claimed that an unsymmetrical structure must be assigned to the disulphoxides. Two unsymmetrical formulæ have been advocated, the thiolsulphonate and the anhydride arrangements (II and III); there is ample reason for discarding the latter (Fries, *loc. cit.*), whilst the former accords very closely with all the facts since discovered.

<p align="center">E X P E R I M E N T A L.</p>

The disulphoxides were obtained, those containing similar aromatic groups from the sulphinic acids by the usual method, and those with dissimilar groups by the reaction of a silver sulphinate with the requisite sulphur chloride as follows. A solution of the sulphur halide in dry ether was shaken at the ordinary temperature or boiled with an excess of the silver sulphinate until all the sulphur halide had disappeared, the treatment being adapted to the reactivity of the materials and the stability of the sulphur halide used. Generally, the disulphoxide separated as the reaction proceeded; when this was complete, the solid material was collected and the disulphoxide was extracted from it with a suitable solvent. In the majority of the cases studied, the yields were good. The following substances were obtained by this method from the stated components.

2-*Nitrophenyl 4-toluenethiolsulphonate*, $O_2N \cdot C_6H_4 \cdot S \cdot SO_2 \cdot C_6H_4Me$, from *o*-nitrophenylsulphur chloride and silver toluenesulphinate, formed colourless prisms, m. p. 97°, soluble in the usual organic solvents (Found : S = 20·7; C = 50·0; H = 3·7. $C_{13}H_{11}O_4NS_2$ requires S = 20·69; C = 50·55; H = 3·58 %). The alcoholic solution of this substance became blue on addition of aqueous sodium hydroxide.

2-*Nitrophenyl 4-chlorobenzenethiolsulphonate*,
<p align="center">$O_2N \cdot C_6H_4 \cdot S \cdot SO_2 \cdot C_6H_4Cl$,</p>
from *o*-nitrophenylsulphur chloride and silver *p*-chlorobenzene-sulphinate, formed colourless prisms, m. p. 123°, soluble in the usual organic media (Found : S = 19·6; Cl = 10·5; C = 43·3; H = 2·66. $C_{12}H_8O_4NClS_2$ requires S = 19·42; Cl = 10·74; C = 43·68; H = 2·44 %).

2-*Nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate*,
<p align="center">$O_2N \cdot C_6H_4 \cdot S \cdot SO_2 \cdot C_6H_3Cl_2$,</p>
from *o*-nitrophenylsulphur chloride and silver 2 : 5-dichlorobenzene-sulphinate, melted at 142° and was sparingly soluble in common

solvents (Found : Cl = 19·4; S = 17·6. $C_{12}H_7O_4NCl_2S_2$ requires
Cl = 19·47; S = 17·61 %).   Like the foregoing disulphoxides,
this substance gave a deep blue solution with alcoholic sodium
hydroxide.

2 : 5-*Dichlorophenyl 2-nitrobenzenethiolsulphonate,*

$$C_6H_3Cl_2 \cdot S \cdot SO_2 \cdot C_6H_4 \cdot NO_2,$$

from silver o-nitrobenzenesulphinate and 2 : 5-dichlorophenyl-
sulphur chloride, separated from hot alcohol in colourless needles,
m. p. 129° (Found : S = 17·6; Cl = 19·6. $C_{12}H_7O_4NCl_2S_2$ requires
S = 17·6; Cl = 19·47 %); aqueous sodium hydroxide added to
the alcoholic solution did not give the characteristic blue colour.
A mixture of the two isomeric substances in approximately equal
amounts melted indefinitely between 88—95°.

2 : 5-*Dichlorophenyl 2 : 5-dibromobenzenethiolsulphonate,*

$$C_6H_3Cl_2 \cdot S \cdot SO_2 \cdot C_6H_3Br_2,$$

from 2 : 5-dichlorophenylsulphur chloride and silver 2 : 5-dibromo-
benzenesulphinate, separated from alcohol in colourless needles,
m. p. 119° (Found : S = 13·8; Cl + Br = 48·3. $C_{12}H_6O_2Cl_2Br_2S_2$
requires S = 13·45; Cl + Br = 48·38 %).

2 : 5-*Dibromophenyl 2 : 5-dichlorobenzenethiolsulphonate,*

$$C_6H_3Br_2 \cdot S \cdot SO_2 \cdot C_6H_3Cl_2,$$
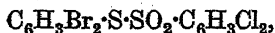
from silver 2 : 5-dichlorobenzenesulphinate and 2 : 5-dibromo-
phenylsulphur bromide, separated from hot alcohol in colourless
prisms, m. p. 125.°   This melting point remained unaltered after a
sample had been fused and cooled.   The substance is less soluble
than the isomeric disulphoxide, and a mixture of the two in approxi-
mately equal amounts melted indefinitely at 110—114° (Found :
S = 13·4; Cl + Br = 48·5. $C_{12}H_6O_2Cl_2Br_2S_2$ requires S = 13·45;
Cl + Br = 48·38 %).

2 : 5-*Dichlorophenylsulphur chloride,* $C_6H_3Cl_2 \cdot SCl$, was prepared by
saturating a concentrated solution of the corresponding disulphide
in dry carbon tetrachloride with chlorine.   The residue obtained
after the solvent had been evaporated was kept under diminished
pressure, when it solidified.   The product was purified by crystallis-
ation from ice-cold ether, when the substance was obtained in golden-
yellow needles, m. p. 32—33° (Found : Cl = 49·8; S = 14·9.
$C_6H_3Cl_3S$ requires Cl = 49·8; S = 15·03 %).   The substance was
very soluble in organic media; dilute aqueous sodium hydroxide
gave the corresponding disulphide and alkali sulphinate.   The
2 : 5-dibromophenylsulphur bromide was obtained by a similar
process as a yellow, crystalline material, but owing to its instability
attempts to isolate it in a pure condition for analysis were un-
successful, some loss of bromine occurring with formation of the
disulphide.

Behaviour of Disulphoxides with Methyl and Phenyl Magnesium Halides.—A dilute solution of the disulphoxide in ether was added to a cooled solution of the magnesium compound (1 mol.) in the

Disulphoxide.	Magnesium derivative.	Sulphinic acid %.	Other substances observed.
Diphenyl	Methyl	63	Ph·S·Me; PhS·SPh.
Diphenyl	Phenyl	70	Ph·S·Ph; PhS·SPh; Ph·Ph.
Di-p-tolyl	Methyl	87	C_7H_7·S·Me; C_7H_7·S·S·C_7H_7.
Di-p-tolyl	Phenyl	76	C_7H_7·S·Ph; (C_7H_7·S·)$_2$ and Ph·Ph.
Di-p-chlorophenyl	Methyl	90	C_6H_4Cl·S·Me; (C_6H_4Cl·S·)$_2$.
2 : 5 : 2′ : 5′-Tetra-chlorodiphenyl	,,	82	
4 : 4′-Dimethoxy-tolyl 3 : 3′-disul-phoxide	,,	68	MeO·C_6H_4·S·Me; and disul-phide.

same solvent. The mixture was kept for 12 hours before treatment with water. Sufficient aqueous sodium thiosulphate was then added to remove free iodine, if this were present, and finally excess of dilute sulphuric acid. The sulphinic acid was extracted from the ethereal solution with dilute alkali, the substances remaining being separately examined. A summary of the results is given in the foregoing table. The third column shows the approximate per-centages in which the sulphinic acids were isolated. These substances were identified by comparison with authentic samples and by con-version to the methylsulphones, which were similarly compared. The latter have been previously described in literature with the exception of the following.

4-Chlorophenylmethylsulphone, C_6H_4Cl·SO_2·CH_3, colourless needles, m. p. 96°, was obtained by oxidation of the sulphide and by methylation of the sodium sulphinate with methyl sulphate (Found : Cl = 18·7; S = 16·6. $C_7H_7O_2$ClS requires Cl = 18·58; S = 16·8 %).

2 : 5-Dichlorophenylmethylsulphone, $C_6H_3Cl_2$·SO_2·CH_3, prepared in a similar manner, separated from hot water in needles, m. p. 88° (Found : S = 14·0. $C_7H_6O_2Cl_2$S requires S = 14·24 %). The identification of sulphides was generally effected by oxidation to the sulphones.

Action of Mercaptans with Disulphoxides.—The method of opera-tion was similar to that already described (Smiles and Gibson, *loc. cit.*), molecular proportions of the reagents being taken in alcohol. The results are collected in the following table; the third and fourth columns, respectively, show the sulphinic acid and the disulphide which were isolated from the interaction of the stated disulphoxide and mercaptan. The yields of these products were generally of the order of 80% of theory and higher when the sparingly soluble

2 : 2′-dinitrodiphenyl disulphide was dealt with. The numerals in the first column refer to numbered formulæ.

Disulphoxide.	Mercaptan.	Sulphinic acid.	Disulphide.
2-Nitrophenyl 4-toluenethiol-sulphonate (VIII)	2-Nitrophenyl	4-Toluene-	Di-o-nitrophenyl
2-Nitrophenyl 4-chlorobenzene-thiolsulphonate (IX)	,,	4-Chlorobenzene-	,,
2-Nitrophenyl 2 : 5-dichloro-benzenethiol-sulphonate (XI)	,,	2 : 5-Dichloro-benzene-	,,
2 : 5-Dichloro-phenyl 2-nitro-benzenethiol-sulphonate (XII)	2 : 5-Dichloro-phenyl	2-Nitrobenzene-	2 : 5 : 2′ : 5′-Tetra-chlorodiphenyl
2 : 5-Dichloro-phenyl 2-nitro-benzenethiol-sulphonate (XII)	2-Nitrophenyl	,,	A mixture : not separated
2 : 5-Dichloro-phenyl 2 : 5-di-bromobenzene-thiolsulphonate (XIII)	2 : 5-Dichloro-phenyl	2 : 5-Dibromo-benzene-	2 : 5 : 2′ : 5′-Tetra-chlorodiphenyl
2 : 5-Dibromo-phenyl 2 : 5-di-chlorobenzene-thiolsulphonate (XIV)	2 : 5-Dibromo-phenyl	2 : 5-Dichloro-benzene-	2 : 5 : 2′ : 5′-Tetra-bromodiphenyl

Reduction of Disulphoxides.—Three methods of reduction were employed. In cases 1, 2, and 3 of the following table, where complete reduction with hydrogen iodide was required, the conditions devised by Hinsberg (*Ber.*, 1908, **41**, 4295) were used. Milder reduction with this reagent was effected as follows. About 2 g. of the disulphoxide, 3—4 c.c. of glacial acetic acid, and a few c.c. of a saturated solution of sodium bisulphite containing ten drops of hydriodic acid (*d* 1·9) were constantly shaken with 50—100 c.c. of light petroleum for about ½ hour, the necessary time varying somewhat according to the disulphoxide taken. Then aqueous sodium carbonate was added until the whole was alkaline. In cases where the dinitro-disulphide was formed, this separated almost completely from the liquid. The solid material was collected, the petroleum and the aqueous portion of the liquid being separately examined. The sulphinic acid was isolated from the aqueous portion and the di-sulphide from the solid or the petroleum. Examples of this type of reduction are given in Nos. 4, 5, 6, and 7 of the table. Reduction with sodium hyposulphite was conducted by shaking the disulph-

oxide with a slight excess of a 3—4 % aqueous solution of the reagent to which about 1/10th of its volume of alcohol had been added, the mixture being kept alkaline by the addition of sodium carbonate. The disulphide formed was isolated by solution in ether, whilst the sulphinic acid and mercaptan were obtained from the aqueous portion. When mercaptan was present, this was separated from the sulphinic acid as disulphide by treating the solution of sodium salts with a current of air. Examples are shown in Nos. 8, 9, and 10 of the table.

Disulphoxide.	Products isolated.
1. 2-Nitrophenyl 4-toluenethiol-sulphonate	2 : 2'-Dinitrodiphenyl disulphide
2. 2-Nitrophenyl 4-chlorobenzene-thiolsulphonate	2 : 2'-Dinitrodiphenyl disulphide and 4 : 4'-dichlorodiphenyl disulphide
3. 2 : 5-Dichlorophenyl 2-nitro-benzenethiolsulphonate	A mixture of disulphides; not separated
4. 2-Nitrophenyl 4-toluenethiol-sulphonate	4-Toluenesulphinic acid and 2 : 2'-di-nitrodiphenyl disulphide
5. 2-Nitrophenyl 4-chlorobenzene-thiolsulphonate	4-Chlorobenzenesulphinic acid and 2 : 2'-dinitrodiphenyl disulphide
6. Di-4-chlorophenyl disulphoxide	4-Chlorobenzenesulphinic acid and 4 : 4'-dichlorodiphenyl disulphide
7. 2-Nitrophenyl 2 : 5-dichloro-benzenethiolsulphonate	2 : 5-Dichlorobenzenesulphinic acid and 2 : 2'-dinitrodiphenyl disulphide
8. Di-*p*-tolyl disulphoxide	*p*-Toluenesulphinic acid and *p*-tolyl mercaptan
9. 2 : 5-Dichlorophenyl 2-nitro-benzenethiolsulphonate	2-Nitrobenzenesulphinic acid and 2 : 5 : 2' : 5'-tetrachlorodiphenyl di-sulphide
10. 2-Nitrophenyl 2 : 5-dichloro-benzenethiolsulphonate	2 : 5-Dichlorobenzenesulphinic acid, 2-nitrothiophenol, and the disul-phide

In conclusion, we desire to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in this work. Our thanks are also due to Mr. W. E. Wright for the derivatives of 2 : 5-dibromophenyl mercaptan used in these experiments.

XXXIX.—*Resolution of Chlorosulphoacetic Acid into its Optically Active Components.*

By HILMAR JOHANNES BACKER and WILHELM GERARD BURGERS.

CHLOROSULPHOACETIC acid, $SO_3H \cdot CHCl \cdot CO_2H$, one of the simplest compounds with an asymmetric carbon atom, has hitherto resisted all attempts at optical resolution. Porcher stated (*Bull. Soc. chim.*, 1902, [iii], **27**, 438) that resolution is possible, but Pope and

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Read, repeating his experiments, did not confirm his results and were led " to dismiss them as not in accordance with experiment " (J., 1908, **93**, 794; 1914, **105**, 811).

We have resolved the racemic acid by a method which apparently had not previously been applied to such purposes, namely, by slow crystallisation of alkaloidal salts in the cold.

After a preliminary examination of their solubility, the alkaloid salts of chlorosulphoacetic acid were prepared by treating the sodium salt at room temperature with a soluble salt of the alkaloid in such dilution that crystallisation of the product did not start at once and only a small part was subsequently deposited. Since the solubility of the alkaloid salts was so small that the effect of the active chlorosulphoacetic acid on the rotation was inappreciable, the sodium and ammonium salts were examined.

For purification, the same " cold crystallisation " was used. The alkaloid salt was therefore converted at 0° into the ammonium salt by means of the theoretical quantity of dilute ammonia, the alkaloid was filtered off, and the solution of the ammonium salt was mixed with the alkaloid (as acetate) in such concentration that again only a part of the alkaloid salt crystallised. By means of yohimbine a dextrorotatory ammonium salt was obtained, and an acid of nearly twice the rotation. *l*-Strychnine gave the dextro-rotatory acid, whilst *d*-cinchonine furnished the lævo-component, so that the small rotation we first obtained could not be ascribed to the presence of traces of the alkaloids. The highest, constant value of the molecular rotation was for the acid $[M]_\mathrm{D} = \pm 39°$ and for the neutral ammonium salt $[M]_\mathrm{D} = \pm 20°$.

The acids and their salts gradually racemise in solution at room temperature. Bases accelerate racemisation of the salts. On evaporation, the solutions lose their activity completely. These active acids, therefore, are more stable than fluorochlorobromo-acetic acid, which shows activity only in its alkaloidal salts (Swarts, *Bull. roy. Belg.*, 1896, [iii], **31**, 25), but they do not attain the high stability of chloroiodomethanesulphonic acid, which is not racemised by any of the usual methods (Pope and Read, *loc. cit.*).*

<center>EXPERIMENTAL.</center>

Preparation of Chlorosulphoacetic Acid.—The method used for the preparation of other sulphocarboxylic acids (*Rec. trav. chim.*, 1920, **39**, 694; 1924, **43**, 297) gives a good yield and a pure product.

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* This research is being continued and the method will be applied to other resolutions. The present results are published because of the departure of Mr. Burgers.—H. J. B.

To 94 g. (1 mol.) of freshly distilled chloroacetic acid, cooled with ice, are gradually added 80 g. (1 mol.) of sulphur trioxide with constant shaking. A viscous, nearly colourless syrup of the mixed anhydride of sulphuric and chloroacetic acids is formed (Found by titration after decomposition with water : equiv. = 57. $CH_2Cl\cdot CO\cdot O\cdot SO_3H$, decomposed by water into $CH_2Cl\cdot CO_2H + H_2SO_4$, requires a mean equivalent weight of $174\cdot5/3 = 58\cdot2$). The anhydride is converted into the sulphonic acid by warming : $CH_2Cl\cdot CO\cdot O\cdot SO_3H \longrightarrow SO_3H\cdot CHCl\cdot CO_2H$. At 70° the external heating is discontinued; the heat of reaction causes the temperature to rise to about 140°, the liquid becoming coloured towards 100° and a feeble evolution of gas (CO_2 and SO_2) setting in. The product is a brown syrup, consisting mainly of chlorosulphoacetic acid (Found : equiv. = 84. Calc. equiv. = $174\cdot5/2 = 87\cdot2$). When kept over-night, the acid may crystallise.

A solution of the syrup or crystallised mass in 5 litres of water is treated with barium carbonate in excess (200 g.). The filtrate, evaporated to 250 c.c. and cooled, deposits 270 g. of pure crystalline barium chlorosulphoacetate (yield more than 80%) (Found : Ba = $41\cdot83$, $41\cdot84$. Calc., Ba = $41\cdot89\%$). On concentration, the mother-liquor gives, as in Andreasch's preparation (*Monatsh.*, 1886, **7**, 158), crystals of barium chloromethanedisulphonate (about 15 g.) (Found : $H_2O = 17\cdot37$; Ba = $32\cdot56$, $32\cdot54$. Calc. for $CHO_6ClS_2Ba,4H_2O$, $H_2O = 17\cdot24$; Ba = $32\cdot86\%$).

Chlorosulphoacetic acid was prepared by shaking its barium salt mechanically for 1 hour with the calculated quantity of $2N$-sulphuric acid. The filtrate, which was free from sulphuric acid and barium, was concentrated first by distillation under reduced pressure, then in a desiccator over sulphuric acid, and finally over phosphorus pentoxide until crystallisation set in.

Chlorosulphoacetic acid forms very hygroscopic crystals containing $1H_2O$ (Found : $M = 191\cdot8$. Calc. for $C_2H_3O_5ClS,H_2O$, $M = 192\cdot56$). The melting point, determined in an apparatus for hygroscopic substances (*Chem. Weekblad*, 1919, **16**, 1564), was 83°.

Normal Alkaloidal Salts.—The normal salts of chlorosulphoacetic acid with various alkaloids were prepared either by dissolving the bases in the equivalent quantity of the acid, or by double decomposition from sodium chlorosulphoacetate with a soluble salt, usually the acetate or phosphate, of the alkaloid. The salts, all of which were obtained in the crystalline state,* were titrated with sodium hydroxide in presence of phenolphthalein or thymolphthalein.

* Pope and Read state that the quinine and cinchonine salts were not obtained crystalline. Their strychnine salt contained $1H_2O$.

The normal *quinine* salt forms a felted mass of small needles containing $4H_2O$ (Found : $H_2O = 8.03$; $M = 894$.

$$C_2H_3O_5ClS,2C_{20}H_{24}O_2N_2,4H_2O$$

requires $H_2O = 8.05\%$; $M = 895.0$).

The normal *cinchonine* salt crystallises with $1H_2O$ in silky needles, concentrically arranged in dense globules (Found : $H_2O = 2.36$; $M = 780$. $C_2H_3O_5ClS,2C_{19}H_{22}ON_2,H_2O$ requires $H_2O = 2.31\%$; $M = 780.9$).

The normal *strychnine* salt, when crystallised from a dilute solution, forms needles, about $\frac{1}{4}$ inch long, containing $3H_2O$ (Found : $H_2O = 6.08$, 6.15; $M = 896.7$, 897.2, 895.8.

$$C_2H_3O_5ClS,2C_{21}H_{22}O_2N_2,3H_2O$$

requires $H_2O = 6.03\%$; $M = 897$).

d-*Chlorosulphoacetic Acid.*—Sodium chlorosulphoacetate (0.05 mol.) in 1150 c.c. of water was treated with 33.4 g. (0.1 mol.) of strychnine dissolved in the same volume of water containing 11 g. of acetic acid. Slender needles began to separate within 1 hour, and after 10 hours, at 20°, 9 g. of strychnine salt were collected, corresponding to 20% of the quantity formed (44.8 g.).

For polarimetric examination, weighed quantities of the strychnine salt (0.5—2 g.) were shaken at 0° with the theoretical quantity of dilute ammonia, the volume was brought to 20 c.c., and the solution of the ammonium salt, after being extracted four times with half its volume of chloroform, was examined by means of a polarimeter (Schmidt and Haensch) with monochromator. In some cases, the concentration of the ammonium salt was verified by evaporation of the solution. The rotatory power was measured for $\lambda = 589$ $\mu\mu$ (D) and for two arbitrary wave-lengths in the green ($\lambda = 533$ $\mu\mu$) and blue ($\lambda = 494$ $\mu\mu$). The ammonium salt, prepared from the strychnine salt mentioned above, gave the following figures : Concentration 0.00480 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = + 0.18°$; $[M]_D = + 18.7°$.

For recrystallisation, 4.48 g. (0.005 mol.) of the active strychnine salt were decomposed by ammonia. The separated strychnine was dissolved in dilute acetic acid and added to the solution of the ammonium salt. The total volume being 230 c.c., the concentration was the same as above. 1.3 Grams, or nearly 30%, separated. Rotation of the ammonium salt : Conc. 0.01115 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = + 0.45°$, $\alpha_{533} = + 0.58°$, $\alpha_{494} = + 0.74°$; $[M]_D = + 20.2°$, $[M]_{533} = + 26.0°$, $[M]_{494} = + 33.2°$. Conc. 0.00560 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = + 0.23°$, $\alpha_{533} = + 0.30°$, $\alpha_{494} = + 0.37°$; $[M]_D = + 20.5°$, $[M]_{533} = + 26.8°$, $[M]_{494} = + 33.0°$.

Addition of sulphuric acid to liberate the acid (2 mols. for 1 mol. of ammonium salt) increased the rotatory power, but this did not change

further on addition of more sulphuric acid.   Rotation of the free acid :
Conc. 0·005 g.-mol. in 100 c.c.; $l = 2$; $\alpha_D = + 0·40°$, $\alpha_{533} = + 0·52°$,
$\alpha_{494} = + 0·62°$; $[M]_D = + 40°$, $[M]_{533} = + 52°$, $[M]_{494} = + 62°$.

l-*Chlorosulphoacetic Acid.*—Sodium chlorosulphoacetate (0·05
mol.) was mixed with 30 g. (0·1 mol.) of cinchonine dissolved in
water containing 9 g. of acetic acid.   The total volume was
1150 c.c.   After 2 days, 5·5 g. of the cinchonine salt, or 14% of
the total amount (39 g.), had separated.

The product was decomposed with ammonia like the strychnine
salt, the only difference being that the alkaloid was filtered off
before extraction of the solution with chloroform.   Rotation of
the ammonium salt :   Conc. 0·00278 g.-mol. in 100 c.c.; $l = 2$;
$\alpha_D = - 0·08°$; $[M]_D = - 14·4°$.

The active cinchonine salt (3·9 g.; 0·005 mol.) was recrystallised
in the same way as the strychnine salt.   From 115 c.c., the same
concentration as above, there separated 0·95 g. or 25%.   Rotatory
power of the ammonium salt :   Conc. 0·00324 g.-mol. in 100 c.c.;
$l = 2$; $\alpha_D = - 0·12°$, $\alpha_{533} = - 0·17°$, $\alpha_{494} = - 0·23°$; $[M]_D = - 18·5°$, $[M]_{533} = - 26·2°$, $[M]_{494} = - 35·5°$.

The acid liberated by an excess of sulphuric acid gave the figures:
Conc. 0·00305 g.-mol. in 100 c.c.; $\alpha_D = - 0·23°$, $\alpha_{533} = - 0·29°$,
$\alpha_{494} = - 0·38°$; $[M]_D = - 37·7°$, $[M]_{533} = - 47·5°$, $[M]_{494} = - 62·3°$.

Thus the mean values for the rotatory power are :

Chlorosulphoacetic acid: $[M]_D = \pm 39°$, $[M]_{533} = \pm 50°$,
$[M]_{494} = \pm 62°$.

Neutral ammonium salt: $[M]_D = \pm 20°$, $[M]_{533} = \pm 26°$,
$[M]_{494} = \pm 34°$.

Racemisation.

The rotation of a neutral solution of the *d*-ammonium salt contain-
ing 0·1 mol. per litre had fallen in a fortnight to half its value.   The
rotation of a solution containing 0·05 mol. of the *d*-acid per litre and
an excess of sulphuric acid diminished in 10 days by one-fourth.

A solution of 0·05 mol. of the ammonium salt per litre containing
0·1 mol. of free ammonia had lost one-third of its rotatory power
within 24 hours.   Examined a week later, it was inactive.

The *d*-acid and the *d*-ammonium salt, each in a solution containing
0·05 mol. per litre, were rapidly heated, boiled for 1 minute, and
immediately cooled.   Their rotatory powers had decreased by
about 5%.   The same solutions, evaporated on a water-bath and
diluted to the original volume, racemised completely.

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XL. — *The Rotatory Dispersive Power of Organic Compounds. Part XIV. Simple Dispersion in 1-Methylcyclohexylidene-4-acetic Acid.*

By Evan Matthew Richards and Thomas Martin Lowry.

Special interest attaches to the rotatory dispersion of centro-asymmetric compounds, which (according to the ordinary definition) contain no asymmetric atom. Through the kindness of Professor Pope we have recently had the opportunity of studying from this point of view his own specimens (compare J., 1909, 95, 1789) of the *d*- and *l*-forms of the well-known acid,

$$\mathrm{CH_3{>}C{<}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}{>}C{=}C{<}^{H}_{CO \cdot OH}.}$$

On Professor Pope's recommendation, the measurements were made with solutions in methylal. The volatility of this solvent made it necessary to express the results in the form of dispersion-ratios, instead of by means of specific or molecular rotations, since the solutions were originally cloudy and their concentrations were altered appreciably by filtration; but we had the very great advantage of being able (except in the photographic region) to read a dextro against a lævo solution, under precisely similar conditions, without being compelled to make use of zero-readings. In these circumstances, a very satisfactory agreement was obtained between the results recorded in two complete series of independent readings.

The data are set out in Table I, together with the corresponding dispersion-ratios calculated from the equation $\alpha/\alpha_{5461} = 0.2422/(\lambda^2 - 0.056)$. Since the value of α_{5461} was about 20° for the visual and 10° for the photographic observations, an error of 0.001 in the dispersion-ratios corresponds with an error of 0.02° in the visual readings, and of 0.01° in the photographic readings.

The largest visual error was therefore about 0.2° (for a difficult dark-blue line) and the largest photographic error about 0.3°. The average error in the visual ratios is 0.003, and in the photographic ratios 0.02; the negative and positive errors are, moreover, distributed in small groups, and afford no evidence of systematic deviations from the formula, such as were observed in the case of octyl oxalate.

The data can be expressed, over the range of wave-lengths covered by our observations and up to the existing limits of experimental accuracy, by one term of Drude's equation. Moreover, since an exposure of more than an hour was required to give the last photographic reading, it is clear that the measurements had been carried right up to the limit of the region of transparency, within

TABLE I.

Dispersion-ratios of 1-Methyl*cyclo*hexylidene-4-acetic Acid in Methylal (about 6 gms. per 100 c.c.) at 20°.* Mol. wt. 154·17.

$$a/a_{5461} = 0.2422/(\lambda^2 - 0.056).$$

| Line. | | Sum of d and l rotations. | | Dispersion-ratios a/a_{5461}. | | | Calc. | Diff. |
		First series.	Second series.	First series.	Second series.	Mean.		
Li	6708	12·81	11·00	0·611	0·602	0·607	0·615	−0·008
Cd	6438	14·20	12·31	0·678	0·674	0·676	0·676	±
Zn	6362	14·53	12·56	0·694	0·688	0·691	0·694	−0·003
Na	5893	17·41	15·20	0·831	0·832	0·832	0·832	±
Cu	5782	18·24	15·91	0·870	0·871	0·871	0·870	+0·001
Hg	5780	18·23	15·88	0·870	0·870	0·870	0·871	−0·001
Cu	5700	18·82	16·45	0·898	0·901	0·900	0·901	−0·001
Hg	5461	20·95	18·26	1·000	1·000	1·000	1·000	±
Cu	5218	23·48	20·47	1·121	1·121	1·121	1·120	+0·001
Cu	5153	24·29	21·19	1·160	1·160	1·160	1·156	+0·004
Cu	5106	24·89	21·64	1·188	1·185	1·187	1·183	+0·004
Cd	5086	25·19	21·85	1·202	1·196	1·199	1·195	+0·004
Zn	4811	28·87	—	1·378	—	1·378	1·381	−0·003
Cd	4800	29·14	25·32	1·391	1·386	1·389	1·389	±
Zn	4722	30·48	26·60	1·455	1·456	1·456	1·450	+0·006
Zn	4680	31·05	27·18	1·482	1·488	1·485	1·486	−0·001
Cd	4678	31·49	27·23	1·503	1·491	1·497	1·487	+0·010
Hg	4358	37·92	32·96	1·810	1·805	1·808	1·808	±

Photographic Series ($a_{5461} = 9.54°$).

| Line. | | Rotation. | Dispersion ratio. | | Diff. |
			Obs.	Calc.	
Fe	4376	*17·11*	1·79	1·79	±
Fe	4337	*17·36*	1·82	1·83	−0·01
Fe	4308	*17·61*	1·85	1·87	−0·02
Fe	4271	*18·11*	1·90	1·92	−0·02
Fe	4261	*18·36*	1·92	1·93	−0·01
Fe	4236	*18·61*	1·95	1·96	−0·01
Fe	4199	*18·98*	1·99	2·01	−0·02
Fe	4187	*19·23*	2·02	2·03	−0·01
Fe	4144	*20·23*	2·12	2·09	+0·03
Fe	4132	*20·36*	2·13	2·11	+0·02
Fe	4119	*20·61*	2·16	2·13	+0·03
Fe	4072	*21·50*	2·23	2·21	+0·02

* The temperature, 20°, was accidentally omitted from the corresponding tables for octyl alcohol and octyl oxalate in Part XII of this series (J., 1924, 125, 1595, 1596). The opportunity may also be taken of correcting an error in Part XI (*ibid.*, p. 1466, two lines from the bottom), where a shallow minimum " at 5 per cent." should be " at 50 per cent." of ethyl tartrate.

which alone Drude's formula is valid. As any deviations disclosed by pushing the observations beyond this limit would be irrelevant to the present discussion, it appears that the simplicity of the dispersion is not likely to be disproved by direct experimental measurements. Complexity could therefore be established only by the use of indirect tests, such as that described in the previous paper

(p. 2511).   In the present instance, however, as in the analogous case of octyl alcohol, this test gives no clear answer to our question, since the characteristic frequency of the dispersion-equation falls in a region in which absorption-bands are very difficult to detect.   Thus the dispersion-constant, $\lambda^2 = 0\cdot056$, of Pope's acid corresponds to a wave-length, $\lambda = 2364$ Å.U., only a little longer than that of the last strong line in the iron arc spectrum.   Direct measurements of the molecular extinction coefficient of the acid in this region (Table II) show, however, that the " general absorption " (log $\epsilon = 3\cdot9$) of the acid at this wave-length is already more than 100 times greater than the maximum selective absorption (log $\epsilon = 1\cdot5$) of camphor and of camphorquinone, at the head of their absorption bands.   It was therefore quite impossible to establish the existence of a band of selective absorption at the wave-length indicated.   In our opinion, however, a negative result of this character does not provide valid evidence that the dispersion is complex; and until some positive evidence to the contrary is available we propose to describe the dispersion of the compound as simple.

<div align="center">TABLE II.</div>

<div align="center">Molecular Extinction Coefficients.</div>

λ	= 2470	2440	2411	2375	2348	2338	2327
log ϵ	= 3·31	3·61	3·78	3·91	4·01	4·09	4·15

The acid contains only one unsaturated group, namely, the conjugated system $>C=CH-C<^O_{OH}$. The characteristic frequency of this is perhaps given by the dispersion-constant of our equation.

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XLI.—*The Electrical Explosion of Tungsten Wires.*

By HENRY VINCENT AIRD BRISCOE, PERCY LUCOCK ROBINSON,
and GEORGE EDWARD STEPHENSON.

THE phenomena accompanying heavy high-tension discharges in thin metallic wires were first studied by Anderson (*Astrophys. J.*, 1920, **51**, 37).   Using a large glass plate and tin-foil condenser, he photographed the spectra of the light emitted by the electrical explosion of iron, copper, nickel, and manganin wires and observed

very interesting effects, notably a reversal of many lines, producing an absorption (Fraunhofer) spectrum instead of the bright-line spectrum usually observed. These phenomena are attributable to the momentary attainment of an exceptionally high temperature in the substance of the wire. Observations with a rotating mirror showed that the duration of the flash was less than 10^{-5} second, and Anderson calculated that if the available energy of his condenser, equivalent to about 30 calories, were wholly communicated to the 2 milligrams of wire in this time, the temperature attained would be of the order of 300,000°. The intrinsic brilliancy of the wire at the moment of explosion was found to correspond with a surface temperature of 20,000°. Making liberal allowance for the inherent uncertainty of these estimates, it seems evident that the temperatures attained in such explosions are much higher than can be reached by any other means.

In 1922, Wendt and Irion (*J. Amer. Chem. Soc.*, **44**, 1887) reported the results of experiments on the explosion of fine tungsten wires by Anderson's method. When the explosions were carried out in a vacuum, some gas was formed, and this, subjected to an ordinary high-tension discharge, gave a spectrum in which the yellow helium line, D_3, was consistently observed. When the wires were exploded in an atmosphere of carbon dioxide at ordinary pressure, and the carbon dioxide afterwards absorbed in caustic potash solution, residual gas, averaging 1·42 c.c. per milligram of tungsten, remained. This gas was lost before its spectrum had been investigated. If it consisted wholly or mainly of helium, it was on the average some 25% of the weight of tungsten taken.

These results were so startling, and, if correct, of such profound significance that the experiments here described were undertaken to confirm them.

The essential idea of these experiments is, of course, extremely simple. A fine tungsten wire is supported between heavy electrodes sealed into a glass vessel; this vessel is evacuated, and a heavy discharge is passed from a condenser of large capacity. Thereafter an ordinary high tension-discharge is passed through a capillary side-tube on the bulb, and the emitted light spectroscopically examined. In practice, the experimental difficulties are considerable and arise chiefly in securing the necessary conditions of very high vacuum and very good contact between the wire and the electrodes. Unless both these conditions are fulfilled, the discharge does not pass through the wire, but passes between the electrodes (possibly through the slight conductivity of gas remaining in the bulbs or produced by local heating of the wire) in such a way that the material of the wire is unaffected.

EXPERIMENTAL.

Preparation of Bulbs.—Three containers, of the form shown in Fig. 1, were first constructed from 300 c.c. spherical Durosil bulbs, A, provided with main electrodes, EE, and a supplementary electrode, F, in a small bulb connected with A by a capillary tube, C. While A was still open at the line D, the wire, W, was sprung into place between EE by means of suitable forceps : thereafter the system of tubes, B G H, was sealed on at D. The electrodes, EE, were of heavy molybdenum wire approximately 0·1 inch in diameter : one end of each was drilled and countersunk with fine drills to receive the filament and they were then coated with glass nearly to the ends and sealed into the bulbs as shown in Fig. 3.
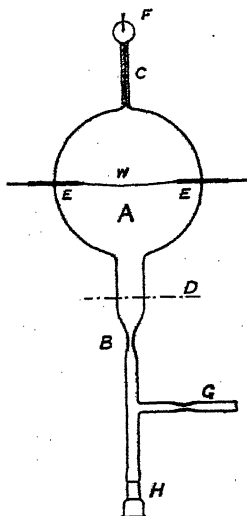
FIG. 1.   FIG. 2.
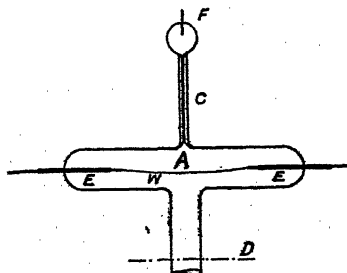
Serious difficulties were encountered in making this apparatus : unless the bulbs were of heavy glass they cracked at the electrode seals and when the seals stood they frequently leaked at pinholes so minute that they could only be detected by a pressure test under water. A T-shaped bulb of about 70 c.c. capacity constructed as in Fig. 2 from Durosil tubing 1″ in diameter proved much more satisfactory.

All attempts to seal heavy tungsten wires into Pyrex glass, as described by Wendt and Irion, failed completely, but, fortunately, it was found that molybdenum sealed fairly well into Durosil glass and could, unlike tungsten, be obtained as drawn wire of the heavy section required to carry the discharge without material loss.

We are indebted to Messrs. Duram Ltd., and to their chemist, Mr. S. C. Radford, who very kindly supplied us with several samples of fine tungsten wire, both hard-drawn and annealed.   The annealed wire proved much less springy and easier to handle than the hard-drawn wire and was used throughout : pieces about 4 cm. long were cut from a soft wire 0·035 mm. in diameter.   It was quite impossible to spring these wires unsupported between the electrodes as Wendt and Irion stated they had done.   With much patience and luck, crystalline filaments from an old drawn-wire lamp could be fitted in this way, but they were so fragile as to be useless in practice.   Therefore the wire was threaded through a very fine and light capillary glass tube, bent back outside the tube at both ends, and then the tube and wire were sprung between the electrodes as shown in Figs. 2 and 3.

Bulbs made as described were connected by the mercury-sealed ground glass joint H (Fig. 1) to a large all-glass Töpler pump and McLeod gauge, and, after a preliminary evacuation by a water-pump connected to G, which was then sealed off at the constriction, were further evacuated with the Töpler pump.   The first bulb was kept at 300° in an electrically heated air-bath, evacuated to 0·005 mm., and left at 300° over-night.   Next

FIG. 3.   FIG. 4.

morning, the pressure in the bulb was 0·02 mm.   This difference appeared to be too large to be accounted for by the release of gases from the glass.   The bulb was allowed to cool and each electrode seal was tested, in turn, by coating it with sealing wax and carrying out a series of evacuations.   By this means it was established that leakage was occurring in the neighbourhood of the seals.   After treating a large surface of the glass with a collodion varnish, a vacuum of 0·001 mm. was maintained over-night.   As a further test of this vacuum, an induction coil discharge was passed between the supplementary electrode and one of the main electrodes : there was at first no visible discharge, but after a time, possibly through the release of gas from the wires or accidental breakage of the wax
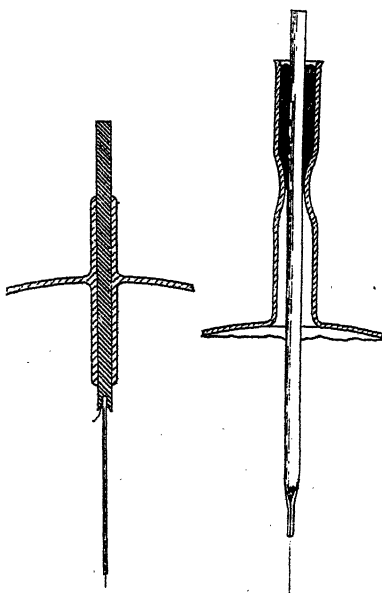
seals, a noisy visible discharge occurred and set up vibration which dislodged the wire and capillary and so rendered the bulb useless.

The details given above for one case will serve to indicate the difficulties attendant on the use of molybdenum–glass seals : As a result of a series of experiments, another metal–glass seal was tried, which promised to be more satisfactory, because, *inter alia*, it permitted the proper support of a naked wire inside the bulb. The essential features of this seal are shown in Fig. 4. The glass tube was constricted to allow the tinned copper electrode to pass through neatly without play. The upper part of the glass was heated nearly to redness and molten lead poured into the tube; the lead chilled so quickly at the constriction that it solidified there and prevented passage of lead into the bulb. The preliminary tests were carried out on single joints, which were sealed to the pump and evacuated. It is interesting to observe that where the glass had been hot, lead which had overflowed on the outside of the tube adhered strongly to the glass and at the colder portions of the tube the lead peeled off quite easily.

After some practice, a satisfactory seal was obtainable and a T-shaped bulb was constructed using this type of joint for the electrode seals. In this bulb the tungsten wire was stretched between the two electrodes and a supporting capillary tube was unnecessary.

One end of each copper electrode was hammered flat and folded into a small trough; then the end of the wire was laid along the trough and secured by hammering the sides together. Good electrical contact and a secure hold for the wire were thus obtained. The electrode and wire were passed through one side tube of the bulb; the upper electrode was then sealed in with molten lead, and finally the bulb was reversed and the second electrode similarly sealed in. This bulb was connected to the pump and evacuated; the following figures show the efficiency of the seals.

28/12/23   4 p.m.   Pressure = 0·0003 mm. of mercury.
8/1/24   10 a.m.   Pressure = 0·0080   ,,   ,,   ,,

Thus these seals, while useful for many purposes, did not appear tight enough for the present experiments.

At this stage it was decided to conduct several explosions, using the highest vacuum attainable, with a number of bulbs, having molybdenum–glass seals, which had been prepared. The electrode seals were coated externally with sealing wax in such a manner as to give an even, well melted coating of wax : such coatings had been found to enable the bulbs to hold very high vacua, and were really excellent except that they precluded strong heating of the bulb during evacuation. A bulb was evacuated to the limit of the pump,

being heated meanwhile to about 100° by means of a soft, luminous gas flame. The evacuated bulb was allowed to stand over-night on the pump, and the state of the vacuum noted. In each case a single stroke of the pump removed a minute bubble, so small that it could not be driven down the capillary fall-tube of the pump. The bulb was again heated and another stroke of the pump showed that no gas had been released from the glass : it was then sealed off at the vertical capillary.

The Explosions.

Messrs. A. Reyrolle & Co. Ltd., electrical engineers, of Hebburn-upon-Tyne, very courteously placed their high-tension testing plant at our disposal and we desire to record here our thanks to Mr. H. W. Clothier and Mr. Harle for their interest and active co-operation in carrying out the experiments at their works.

Fig. 5.
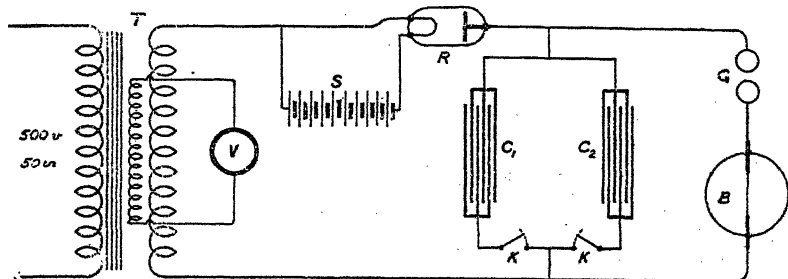
Fig. 5 is a diagram of the circuit used. The two condensers, C_1 C_2, each consisted of 100 glass plates, 24 inches square, having on each face tinfoil coatings 18 inches by 17 inches : the plates were carried on porcelain insulators in a wooden frame : heavy brass leads connected alternate coatings with two copper busbars on opposite sides of the condenser. The condensers were not oil-immersed. Each had a capacity of 0·3 microfarad, the normal working pressure was 30,000 volts, and the highest permissible pressure was 45,000 volts. The connexions permitted the use of either condenser singly or of both in parallel.

Current at 500 volts and 50 cycles A.C. from the supply mains fed to the transformer, T, was stepped up to any desired voltage (up to a maximum of 100,000 volts) and the output was rectified by a two-electrode thermionic valve, R, the filament current for which was supplied by the accumulator, S. The knife switches, K, being closed, this rectified output charged the condensers. When the potential difference across the condensers reached a certain

value dependent on the width of the adjustable air-gap, G, between two large polished brass spheres, the condensers discharged across the gap and through the bulb B. The whole of this apparatus was contained in a large cage of expanded steel, well earthed, and the necessary switches were actuated from the outside of the cage.

A kilovoltmeter, V, across a tertiary winding of the transformer gave an approximate indication of the discharge potential. Throughout the experiments the spark-gap was kept constant and at the conclusion of the tests a precise measurement showed that the potential difference required for discharge across the gap was 29,000 volts.

In one case, contact between the leads and the electrodes of the bulb was made through mercury contained in rubber tubing slipped over the latter. This bulb fractured on discharge, probably because this method of securing contact was defective, and the other bulbs were connected up in turn by twisting the leads tightly round the external parts of the electrodes.

The phenomena associated with the explosions may best be described by giving the details with reference to one of the several bulbs exploded. Bulb No. 4 was spherical, had molybdenum electrodes sealed in through the glass and a filament fitted in a capillary tube as already described. Both condensers were used connected in parallel, giving a total capacity of 0·6 microfarad. At discharge, the kilovoltmeter, K, indicated 30,000 volts. The air-gap was screened from sight and the explosion was well seen by four observers : it was attended by a dull thud in the bulb, and by a bright flash in which the whole of the filament was seen to be involved. Both the noise and the brightness of the flash were much less than we had anticipated.

On examining the bulb, it was found that the filament had completely disappeared : the capillary, now loose in the bulb, was intact, showed a mere trace of a metallic mirror at one end, and was slightly bent at both ends, having evidently been softened there by heat.

It will be remarked that these effects differ substantially from those described by Wendt and Irion : we nevertheless regarded this explosion as complete and satisfactory.

Within a few hours after explosion, the contents of the bulbs were investigated. An induction coil discharge was passed between the supplementary electrode, F, and one of the main electrodes, and the light emitted in the capillary tube, C, was examined visually with a Hilger constant deviation spectrometer. In each of the bulbs there was a small amount of gas which permitted a discharge to pass and gave a faint banded spectrum on which were superposed a few bright lines, the wave-lengths of which were read directly

on the spectrometer drum. The lines observed were the green lines of mercury and the red and blue hydrogen lines; none of the bulbs at any time gave any yellow line whatever, although the spectrometer showed the two sodium lines bright and well defined in the light from an ordinary Bunsen flame.

We conclude, therefore, that our experiments afford no evidence that tungsten can be made to yield helium when exploded by an electrical discharge. At the same time, it is clear that extreme difficulties attend any attempt at a crucial experiment on these lines, and we attach much more importance to experiments now in progress on the electrical explosion of tungsten wires in relatively dense and non-conducting atmospheres of absorbable gas.

Our conclusion is supported by the results, published since our tests were completed, of a similar series of experiments conducted in Dr. Anderson's laboratory (Sinclair Smith, *Proc. Nat. Acad. Science*, 1924, **10**, 4). This investigator encountered difficulties in the construction of gas-tight containers, and in attaining satisfactory vacua, precisely similar to those we have described, but he finds no evidence of any formation of helium by the electrical explosion of tungsten.

A still more recent publication (Harkins and Allison, *J. Amer. Chem. Soc.*, 1924, **46**, 814) describes experiments in which heavy electrical discharges were passed (a) *between* fine wire electrodes, and (b) through fine metallic wires, and the gases (if any) were examined for helium by absorption in heated metallic calcium by Soddy's method. In most cases, the gas was completely absorbed and in no case was there any evidence of helium. Hence it seems clear that the statements made by Wendt and Irion must be attributed to erroneous observations and have no foundation in fact.

XLII.—*Physostigmine (Eserine). Part III.*

By EDGAR STEDMAN and GEORGE BARGER.

CERTAIN details of the structure of physostigmine have been elucidated (J., 1923, **123**, 758; 1924, **125**, 1373), but the evidence which was available was insufficient to permit the construction of

a formula which satisfactorily represented the known facts concerning the chemistry of this alkaloid. Further experimental evidence is now advanced, and this, combined with previously published work, appears to leave no doubt as to the structure of eserethole and hence of physostigmine, which are respectively the ethyl ether and methylcarbamido-derivative of eseroline.

The presence in eseroline of the grouping I has been recognised
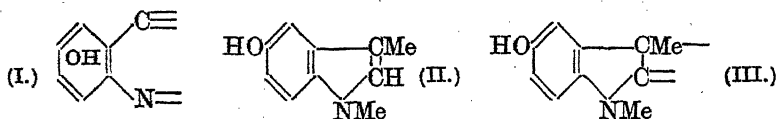
since the work of Straus (*Annalen*, 1913, **401**, 350; 1914, **406**, 332), who obtained a phenolic indole compound (physostigmol) by degradation of eseroline methiodide. It was shown by one of us (E. S.; *loc. cit.*, 1373) that physostigmol is 5-hydroxy-1 : 3-dimethyl-indole (II), and further that its ethyl ether may be obtained in a yield of 66% by distillation of eserethole methiodide. This established the position of the hydroxyl group in eseroline and also confirmed Straus's supposition that physostigmol contains a methyl group attached to position 3 of the indole ring. The formation of an indole compound by the somewhat violent decomposition of an alkaloid does not, in general, permit the conclusion to be drawn that a preformed indole skeleton exists in the latter. Nevertheless, it appears justifiable, in view of the comparative completeness with which eserethole methiodide is degraded into physostigmol ethyl ether, to assume, even without further evidence, the presence of the grouping III in eseroline. Additional evidence pointing to the presence of an indoline grouping in the molecule is not, however, wanting. Thus, the feebly basic properties of one of the nitrogen atoms in physostigmine (Straus, *loc. cit.*) and the properties of etheserolene, obtained by Max and Michel Polonovski (*Bull. Soc. chim.*, 1918, [iv], **23**, 335; 1923, [iv], **33**, 969) by the exhaustive methylation of eserethole, point in this direction.

The presence of the grouping III may thus be regarded as established, and the problem resolves itself into determining the manner in which the remainder of the molecule (C_3H_8N) is linked to this grouping. The nitrogen atom, the position of which has still to be determined, is the one with the stronger basic properties. Straus has shown that one methyl group is attached to this nitrogen atom, whilst Salway (J., 1912, **101**, 978) had previously demonstrated its tertiary character. Formula IV, which was suggested to us by Professor R. Robinson, F.R.S., conforms to these conditions, and evidence will be adduced in the following discussion

to show that this actually represents the structure of eseroline. The constitution of physostigmine itself will accordingly be represented by formula V.

(IV.) HO—[benzene ring]—C(Me)(CH$_2$)—CH$_2$—CH—NMe / NMe   NHMe·CO·O—[benzene ring]—C(Me)(CH$_2$)—CH$_2$—CH—NMe / NMe (V.)
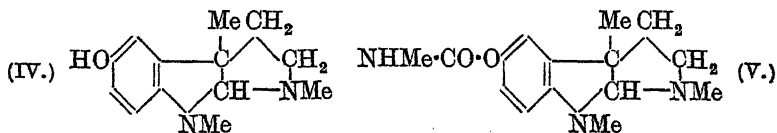
The considerations which have led to the adoption of formula IV for eseroline are largely based on the behaviour of eserethole towards reducing agents and on the properties of eseretholemethine. Polonovski (*Bull. Soc. chim.*, 1918, [iv], **23**, 357) has shown that eserethole, on reduction with zinc and hydrochloric acid, takes up two atoms of hydrogen, a result which has now been confirmed using a catalytic method of reduction. That this reduction is not due to the presence of a double bond follows from the fact, first pointed out by Max and Michel Polonovski (*Compt. rend.*, 1924, **178**, 2078), that, whereas eserethole is a tertiary base, dihydroeserethole is a secondary base. Reduction evidently opens a ring between the more strongly basic nitrogen atom and one of its adjacent carbon atoms. On the basis of IV, dihydroeserethole may thus be represented by VI, the point at which the ring is ruptured being deter-

EtO—[benzene ring]—C(Me)·CH$_2$·CH$_2$·NHMe / CH$_2$ / NMe (VI.)   EtO—[benzene ring]—C(Me)·CH$_2$·CH$_2$·NMe$_2$ / CH·OH / NMe (VII.)
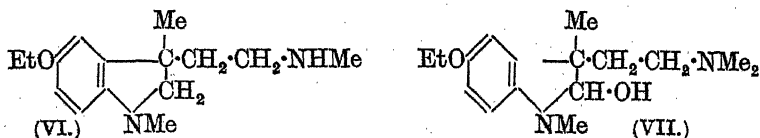
mined from Polonovski's observation that the substance obtained by reduction of etheserolene is identical with the product of the exhaustive methylation of dihydroeserethole.

Eseretholemethine was obtained by Max and Michel Polonovski (*loc. cit.*) by treating eserethole methiodide with sodium hydroxide. Its pseudo-basic character was not recognised until, in Part I of this series, attention was directed to the fact that it is reconverted into eserethole methiodide on treatment with hydriodic acid, and that its behaviour in this respect was analogous to that of certain indoline compounds prepared by Brunner. As a result of this observation, Polonovski revised the molecular formula of eseretholemethine and demonstrated that it was produced from methyleseretholinium hydroxide by a tautomeric change and not by loss of water. Experimental results, which are enumerated in the succeeding paragraph, have now been obtained which demonstrate that eseretholemethine is, in fact, a substituted indoline with a

hydroxyl group in the α-position (VII); its formation may accordingly be represented by the following scheme :

| Eserethole methiodide | Intermediate quaternary hydroxide | Eseretholemethine |
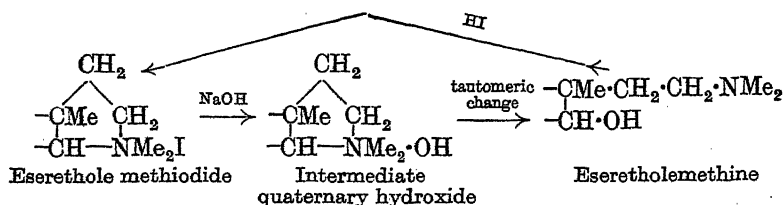
The position assigned to the basic nitrogen atom in V thus corresponds with this behaviour.

Assuming the correctness of this scheme, it is evident that while the conversion of eseretholemethine into a quaternary salt by treatment with methyl iodide should prevent the closure of the pyrrolidine ring on treatment with acids, the compound should nevertheless retain its properties as a pseudo-base in virtue of its indolinol structure. This consequence has been verified. Treatment of eseretholemethine methiodide with picric acid results in the elimination of the hydroxyl group with the formation of a diquaternary picrate :
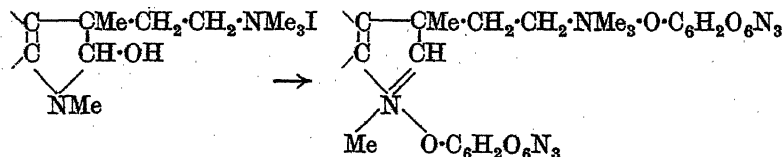
Still more conclusive are the results obtained by oxidation of eseretholemethine. Brunner (*Monatsh.*, 1896, **17**, 253) has shown that 1 : 3 : 3-trimethyl-2-indolinol is oxidised by ammoniacal silver nitrate in alcoholic solution to 1 : 3 : 3-trimethyl-2-indolinone. By subjecting eseretholemethine to the same treatment, a compound the composition of which corresponds with VIII has been obtained. The same substance has also been prepared by oxidising eseretholemethine with potassium ferricyanide, a method which Decker (*J. pr. Chem.*, 1893, **47**, 28) has employed for the oxidation of pseudo-bases. When this compound is degraded by the method of

(VIII.)

(IX.)

(X.)
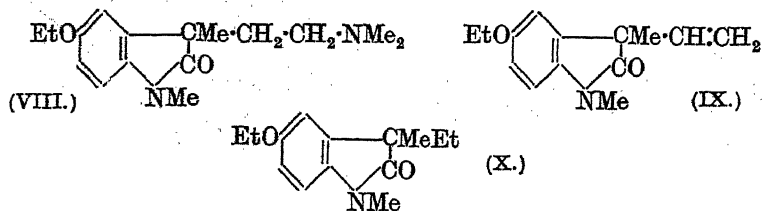
exhaustive methylation, trimethylamine is evolved and an un-saturated compound (IX) obtained which is practically devoid of basic properties and forms a deep crimson picrate. On reduction, this takes up two atoms of hydrogen with the formation of a substance which is considered to be 5-ethoxy-1 : 3-dimethyl-3-ethyl-2-indolinone (X). The chemical properties of eserethole-methine thus correspond entirely with those predicted on the assumption that V correctly represents the structure of physos-tigmine ; the constitution of this alkaloid may therefore be regarded as established. As an additional confirmation, the synthesis of the substance represented by X has been undertaken and it is hoped that it will be possible to communicate the results shortly.

An explanation of the mechanism of the formation of eserethole-methine and of dihydroeserethole identical with that advanced above has recently been put forward by Max and Michel Polonovski (*Compt. rend.*, 1924, **178**, 2078). These authors therefore consider that the structures of eserethole and eseretholemethine are repre-sented by XI and XII, respectively; the former differs from that proposed by Straus (*loc. cit.*) for eseroline only in the position of the nitrogen atom contained in the piperidine ring. Although the reactions described in this communication could be formulated with equal facility upon the basis of these structures, it is evident that they do not explain the formation of physostigmol; the ease with which this substance is formed demands the presence of a preformed methyl group in the β-position of the pyrroline ring.
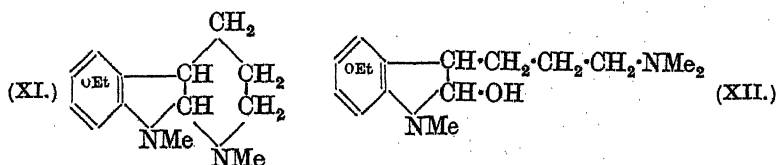
Consideration of the possible mechanism of the phytochemical synthesis of the ring system present in physostigmine speaks no less convincingly in favour of formula V. Perkin and Robinson (J., 1919, **115**, 944) have shown how harmine may be elaborated in the plant from tryptophan. If the assumption is made that the methylation of an indole nucleus may proceed in the plant in the manner in which it is known to take place in the laboratory, a relation between physostigmine and this amino-acid at once becomes evident. By decarboxylation and methylation, followed by a ring closure, the ring system of physostigmine would be readily formed :

$$\text{C·CH}_2\text{·CH(NH}_2\text{)·CO}_2\text{H} \xrightarrow{\text{decarboxylation}} \text{C·CH}_2\text{·CH}_2\text{·NH}_2$$

(indole ring system with CH, NH) ... *methylation* ... *tautomeric change* ... *ring closure*

Me─C·CH$_2$·CH$_2$·NHMe (CH, N, Me OH)

Me─CH$_2$·CH$_2$·NHMe (CH·OH, N, Me)

Me CH$_2$─C─CH$_2$ (CH──NMe, NMe)
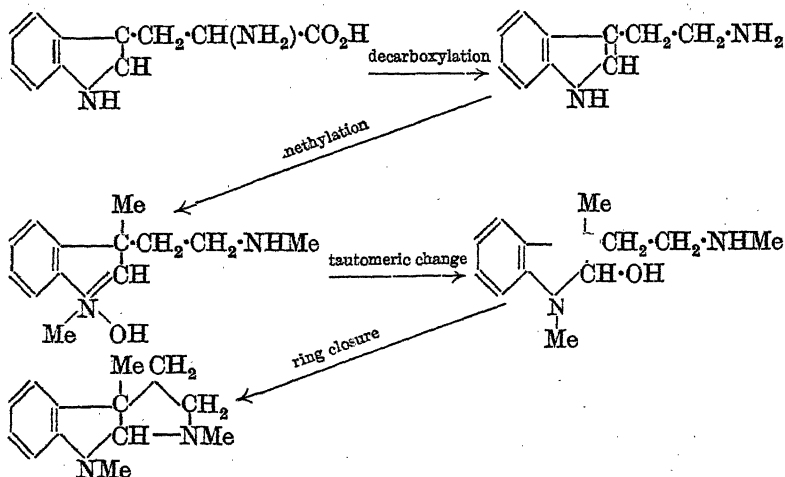
The possible mechanism of the phytochemical synthesis of the ring system present in XI cannot be similarly represented in a simple manner from known naturally-occurring substances.

During the course of this investigation a small quantity of etheserolene was prepared. Contrary to Polonovski's statement, it readily formed a yellow, crystalline picrate. If etheserolene is formed by a straightforward degradation of eserethólemethine in a manner similar to that of the indolinone compound now described, one would feel inclined to attribute to it the structure represented by XIII. On this basis, however, it should possess the properties

(XIII.) EtO─ (benzene ring) ─C·CH:CH$_2$ (CH$_3$, CH·OH, NMe)

EtO, NO$_2$ ─ (benzene ring) ─C (NO$_2$, Me CH$_2$, CH$_2$, CH──NMe, NO$_2$ NMe) (XIV.)
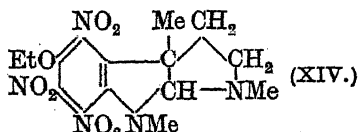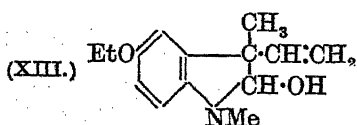
of a pseudo-base. But analysis of the picrate shows that this is not the case. It therefore appears that some isomeric change has taken place during its formation. This would correspond with the results of Polonovski, who has recently stated (*Compt. rend.*, 1924, **179**, 178) that etheserolene, on reduction, absorbs only two atoms of hydrogen and at the same time loses an atom of oxygen. Whether his view that this oxygen atom is not present as a hydroxyl group, but forms part of a ring, is correct, cannot be stated with certainty at present.

Trinitroeserethole (XIV) and an oxidation product of eserethole which have been prepared during the course of this investigation and the results of a reinvestigation of the degradation of one of the

esoline compounds described in Part I of this series are described in the experimental portion.

EXPERIMENTAL.

Dihydroeserethole (VI).—Attempts to reduce eserethole catalytically with a palladium sol in either neutral or acid solution, with or without the addition of gum arabic as protective colloid, were unsuccessful, owing to flocculation of the sol. With platinum black prepared by Willstätter's method (*Ber.*, 1921, **54**, 113), reduction took place readily. Platinum black (0·1 g.) was washed into a hydrogenation apparatus similar to that described by Hess (*Ber.*, 1913, **46**, 3113), air was completely removed, a solution of 1 g. of eserethole in glacial acetic acid introduced, and the mixture shaken; 52 c.c. of hydrogen were absorbed during the first hour, and 92 c.c. in all (calculated for two atoms : 91 c.c.). The solution was filtered, made alkaline with sodium hydroxide, and the oil thus thrown down extracted with ether. From the extract dried over potassium carbonate a yellow oil was obtained which became almost colourless when distilled under the vacuum of a rotatory oil pump (bath at about 200°). When treated with alcoholic oxalic acid, it formed an oxalate (sheaves of fine needles, m. p. 204°, from aqueous alcohol), identical with that obtained from dihydroeserethole prepared by Polonovski's method (*loc. cit.*).

Dihydroeserethole (1 g.) was heated in a sealed tube with excess of methyl iodide for 1 hour at 100°, the excess of methyl iodide evaporated, and an alcoholic solution of the product treated with alcoholic picric acid. The yellow picrate precipitated on addition of water crystallised from aqueous alcohol in prisms, m. p. 204° (Found : C = 47·0; H = 4·7. $C_{29}H_{34}O_{15}N_8$ requires C = 47·3; H = 4·6%). The substance was thus a *dipicrate*, and two methyl groups had been introduced into the molecule during methylation, indicating that, in contrast to eserethole, dihydroeserethole is a secondary base.

Behaviour of Eseretholemethine Methiodide as a ψ-Base.—The orange oil which separated on mixing the salt (0·2 g.) and picric acid in alcoholic solution changed, on warming, into a crystalline solid (0·27 g.), which was obtained from aqueous alcohol in yellow prisms, m. p. 170° (Found : C = 47·7; H = 4·7. $C_{29}H_{32}O_{15}N_8$ requires C = 47·5; H = 4·4%). In the formation of this diquaternary picrate, water has been eliminated from the molecule, thus indicating the pseudo-basic function of the oxygen atom.

Dehydroeseretholemethine (VIII).—The methine (1 g.) was refluxed for 10 hours with an ammoniacal solution of 3 g. of silver nitrate in methyl alcohol. After filtration, evaporation, and dissolution

of the residue in water, ether extracted an insignificant amount of an oil, which formed a crystalline picrate, but was not investigated further. The hot aqueous solution, made faintly alkaline with ammonia, was treated with hydrogen sulphide to remove excess of silver, filtered, boiled to expel ammonia and hydrogen sulphide, and treated with alcoholic picric acid. The viscous precipitate first formed became crystalline on warming and, by fractional crystallisation from aqueous alcohol, gave two picrates, the more soluble one forming needles, m. p. 211° (Found : C = 47·0 ; H = 4·5. $C_{16}H_{26}ON_2,2C_6H_3O_7N_3$ requires C = 46·7 ; H = 4·4%), and the less soluble fraction consisting of plates contaminated with some needles. The latter crystallised from acetone in plates, m. p. 199° (Found : C = 52·8 ; H = 5·4. $C_{16}H_{24}O_2N_2,C_6H_3O_7N_3$ requires C = 52·3 ; H = 5·4%).

A different result was obtained by the following procedure : An alcoholic solution of eseretholemethine (5 g.) was added to 15 g. of silver nitrate in alcohol made strongly alkaline with ammonia (d 0·88), the total volume being brought to about 100 c.c. A silver mirror formed on the sides of the flask almost immediately. The mixture was heated on the water-bath for 5 hours, filtered, and excess of silver removed by addition of hydrochloric acid ; from the filtrate, made alkaline with sodium hydroxide, ether extracted 4·45 g. of an oil which, treated with alcoholic picric acid, yielded 5·35 g. of the picrate, m. p. 199°, described above. No trace of the picrate of higher melting point was obtained in this experiment. It seems evident that this substance was formed by reduction of an indolinone to an indoline compound, the reducing agent being the hydrogen sulphide used to remove excess of silver.

Oxidation was also effected by means of potassium ferricyanide. A solution of eseretholemethine (3 g.) in a small quantity of alcohol was boiled with a strongly alkaline solution of 7·2 g. of potassium ferricyanide in 100 c.c. of water for about 5 minutes and after cooling extracted with ether. From this extract, 4 g. of the methiodide which had previously been prepared in the manner described below were obtained.

The picrate (4·19 g.), m. p. 199°, was treated with sodium hydroxide, and the oily base which separated extracted with ether. The extract was dried over sodium sulphate, filtered, concentrated, and methyl iodide added. A crystalline methiodide slowly formed (3·3 g.). This separated from acetone in transparent prisms, but the method was wasteful owing to its large solubility in this solvent. It was therefore crystallised by addition of dry ether to the acetone solution. With dry solvents, the *methiodide* was obtained as a colourless substance, m. p. about 131° ; the fact that the melting

point was not absolutely sharp was no doubt due to the water of crystallisation which it contained (Found : for air-dried material, $H_2O = 3.7$; for material dried at 110°, $I = 30.0$. $C_{17}H_{27}O_2N_2I,H_2O$ requires $H_2O = 4.1$; $C_{17}H_{27}O_2N_2I$ requires $I = 30.1\%$). When, however, the solvents were not perfectly dry, the transitory formation of a blue iodine adsorption compound was consistently observed; its disappearance no doubt coincided with the transformation of an at first amorphous precipitate into crystalline form.

Degradation of Dehydroeseretholemethine Methiodide by Hofmann's Method to Compound IX.—An aqueous solution of 1·9 g. of the methiodide was shaken with a suspension of silver oxide prepared from 2 g. of silver nitrate. After filtration and removal of the water by evaporation under diminished pressure, the residual oil was distilled at 12 mm. After evident decomposition, with the evolution of a gas, a slightly brown oil distilled when the temperature of the bath was between 200° and 210°. The distillate would not crystallise. It was therefore treated with an alcoholic solution of picric acid, when a small quantity of a crystalline picrate, m. p. 199°, identical with that described above, was obtained. The residue from the mother-liquors was treated with sodium hydroxide and extracted with ether, and the extract washed with water until the sodium picrate was completely removed. After drying over sodium sulphate, the ether was evaporated, when a colourless oil which crystallised spontaneously was obtained. Recrystallised from aqueous alcohol, it formed colourless prisms, m. p. 62° (Found : $C = 72.3$; $H = 7.3$. $C_{14}H_{17}O_2N$ requires $C = 72.7$; $H = 7.4\%$). This substance was practically devoid of basic properties; it was insoluble in dilute hydrochloric acid, but formed a picrate which at first separated from alcohol in a yellow form and quickly changed into a deep crimson one; m. p. 103°.

Reduction of Compound IX to Compound X.—Hydrogenation was effected in the apparatus mentioned above, using a solution of colloidal palladium as catalyst and gum arabic as protective colloid; 0·16 g. of substance was used. Hydrogen was readily absorbed, but as a result of a mishap the amount could not be measured. After filtration from the palladium and evaporation of the alcohol (aqueous alcohol was used as solvent), the solution, after addition of a small quantity of sodium hydroxide to ensure alkalinity, was extracted with ether. After drying and evaporation, this yielded a crystalline product which, when crystallised from aqueous alcohol, formed cubes, m. p. 68° (Found : $C = 71.8$ $H = 8.2$. $C_{14}H_{19}O_2N$ requires $C = 72.1$; $H = 8.2\%$). It is evident from the analysis that two atoms of hydrogen were absorbed and

that the oxygen atom present as a carbonyl group was retained in the molecule.

Trinitroeserethole.—Among the diverse experiments which have been carried out with a view to effect the oxidation of eserethole, the action of nitric acid on this substance has been studied. Cold dilute nitric acid has little, if any, action, but the concentrated acid (d 1·4) reacts vigorously. Eserethole (1 g.) was added drop by drop to 3 c.c. of concentrated nitric acid, cooled in a freezing mixture and vigorously stirred. The product was warmed on the water-bath for ½ hour, cooled, diluted with water, and the yellow crystalline precipitate (0·3 g.) recrystallised from aqueous alcohol, *trinitroeserethole* separating in orange, rectangular plates, m. p. 152° (Found : C = 47·1 ; H = 5·0 ; N = 18·7. $C_{15}H_{19}O_7N_5$ requires C = 47·2 ; H = 5·0 ; N = 18·4%). It is insoluble in alkalis and dilute acids, but dissolves in concentrated acids.

Oxidation of Eserethole with Potassium Permanganate in Acetone Solution.—A solution of eserethole (1 g.) in 100 c.c. of acetone was maintained at about −10° while finely powdered potassium permanganate (representing 6 O) was added during 2 days. The solution was then warmed with methyl alcohol to remove excess of permanganate, filtered, and the solvent evaporated. The red syrup thus obtained would not crystallise even after distillation in a high vacuum, but on treatment with alcoholic picric acid it readily yielded a *picrate* (0·9 g.) which crystallised from alcohol in rhomb-shaped prisms, m. p. 166° (Found : C = 51·8 ; H = 4·9; $C_{15}H_{20}O_2N_2,C_6H_3O_7N_3$ requires C = 51·5 ; H = 4·7%). The base was recovered from this picrate by dissolving the latter in glacial acetic acid, pouring into water, and extracting the picric acid with ether, making alkaline with sodium hydroxide and again extracting with ether. The oily base obtained on evaporation of the ether was warmed with methyl iodide and the product dissolved in hot methyl alcohol. On cooling, the *methiodide* crystallised in needles, m. p. 198—199° (Found : C = 48·1 ; H = 5·8 ; I = 31·6. $C_{15}H_{20}O_2N_2,CH_3I$ requires C = 47·8 ; H = 5·8 ; I = 31·6%). This methiodide resembles eserethole methiodide in its behaviour towards alkalis. It is stable towards sodium carbonate, but when treated with sodium hydroxide yields an ether-soluble base. The latter could not, however, be crystallised, neither could its methiodide be obtained in a crystalline condition.

Etheserolene picrate was prepared incidentally during an experiment designed to test whether the presence of ethyl alcohol or sodium ethoxide was an essential condition for the formation of the esoline compounds described in Part I of this series. Starting from eserethole methiodide, the experimental conditions were

exactly similar to those described in that paper for the preparation of esoline ethyl ether dimethiodide, except that a solution of sodium in n-propyl alcohol was used in place of one in ethyl alcohol. No solid separated, however, from the solution. The propyl alcohol was therefore evaporated, the oily residue dissolved in water, made strongly alkaline with solid sodium hydroxide, and the solution refluxed for several hours, tetramethylammonium iodide and an oil volatile in steam separating. The latter, isolated from the mother-liquors by extraction with ether, crystallised in a few hours. The solid, m. p. about 45° (etheserolene, according to Polonovski, melts at 48°), was dissolved in alcohol and treated with alcoholic picric acid, when a yellow picrate separated which crystallised from alcohol in stout prisms, m. p. 98° (Found : C $= 52.1$; H $= 4.9$. Calc. for $C_{14}H_{19}O_2N$, $C_6H_3O_7N_3$, C $= 52.0$; H $= 4.8\%$). From the melting point of the original substance and the analysis of the picrate, it seems evident that this was etheserolene picrate. It is also evident that the oxygen atom has no pseudo-basic function in this compound.

Degradation of Esoline Ethyl Ether Dimethiodide.—The preliminary results of the degradation of this substance by Hofmann's method reported in Part I of this series have been confirmed. Since identical results have been obtained by distillation of the product of the action of silver oxide on the iodide and by treating it with potassium hydroxide, only the latter method need be described. The oil obtained by treating 4 g. of the iodide with silver oxide was refluxed for $\frac{1}{2}$ hour with 10 c.c. of 50% potassium hydroxide. The solution was then steam-distilled until the oil had been completely carried over. The distillate was extracted with ether, upon evaporation of which an oily residue was obtained. This was dissolved in alcohol and the solution treated with picric acid. A viscous picrate separated which slowly solidified on warming. After filtration, this was suspended in a relatively large volume of alcohol, boiled, and filtered. On cooling the filtrate, a *picrate* separated in short, stout prisms, m. p. 156°, unchanged on recrystallisation from aqueous alcohol (Found : C $= 46.7$; H $= 4.7$. $C_{16}H_{28}ON_2,2C_6H_3O_7N_3$ requires C $= 46.5$; H $= 4.7$. $C_{16}H_{26}ON_2,2C_6H_3O_7N_3$ requires C $= 46.7$; H $= 4.4\%$). The less soluble *picrate*, which was separated in the manner described above, crystallised from aqueous alcohol in rhomb-shaped prisms, m. p. 199° (Found : C $= 46.9$; H $= 4.7$. $C_{18}H_{30}O_2N_2,2C_6H_3O_7N_3$ requires C $= 47.1$; H $= 4.7$. $C_{18}H_{28}O_2N_2,2C_6H_3O_7N_3$ requires C $= 47.2$; H $= 4.5\%$). Both picrates were converted into methiodides by the following treatment. The picrate was dissolved in glacial acetic acid, poured into water, extracted with ether to remove

picric acid, made alkaline with ammonia, and the base extracted with ether. Addition of methyl iodide to the ethereal solution (dried over sodium sulphate) caused the methiodide to separate. The picrate melting at 156° thus yielded a methiodide which crystallised in plates, melted at 169—170°, and was identical with a methiodide which had been obtained directly from the crude product of the distillation of the quaternary hydroxide without purification through the picrate (Found : C = 50·2; H = 7·4. $C_{17}H_{31}ON_2I$ requires C = 50·2; H = 7·6. $C_{17}H_{29}ON_2I$ requires C = 50·5; H = 7·2%). The picrate melting at 199° yielded a methiodide, m. p. 141°; when this was heated at 100° in a sealed tube for $\frac{1}{2}$ hour with excess of methyl iodide, a second methiodide, m. p. 188°, was obtained, but no esoline ethyl ether dimethiodide was formed. Apparently this base was not, as was originally believed, the ethyl ether of the hypothetical esoline base.

XLIII.—The Action of Light on the Ferrous Ferric Iodine Iodide Equilibrium.

By ERIC KEIGHTLEY RIDEAL and EDWARD GARDNER WILLIAMS.

THE exceptions to Einstein's laws of photochemical equivalence may be divided into two classes according as the number of quanta absorbed is (1) greater than the number of molecules decomposed, the excess quanta being emitted as fluorescence or dissipated in heating the reacting system, or (2) less than the number of molecules decomposed. In class (2), chain reactions occur of the atom type as is exemplified in the reactions $Cl + H_2 = HCl + H$ and $H + Cl_2 = HCl + Cl$ (Nernst, Z. Elektrochem., 1918, 24, 335), or the product of the reaction with the original energy of excitation together with the energy liberated by the reaction may excite other molecules on impact (Christiansen and Kramers, Z. physikal. Chem., 1924, 104, 452) as, e.g., in the chorination of toluene at low temperatures without a chlorine carrier (Book and Eggert, Z. Elektrochem., 1923, 340, 521). It is to be anticipated that if a photosensitive system could be formed in which chain reactions of either of these ssort could be eliminated the Einstein law of photochemical equi-

valence would be obeyed. Conditions for such evidently obtain in systems in which the energy may be rapidly dissipated, no atom chains being formed, and in which the energy of excitation is relatively small.

It has long been known that the interaction between ferric salts and iodides to produce ferrous ions and free iodine is reversible and that the reaction expressed by the equation

$$2Fe^{...} + 2I' \underset{\text{light}}{\overset{\text{dark}}{\rightleftarrows}} 2Fe^{..} + I_2$$
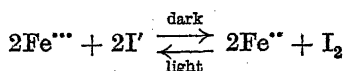
is photosensitive. Sasaki (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 5) has shown more recently that under conditions of uniform illumination with light from an electric lamp a photochemical equilibrium different from the dark equilibrium is attained.

It was considered that this reaction might reasonably be expected to obey the Einstein law of photoequivalence. An investigation of the photodynamics of the system revealed the fact that this law was rigidly fulfilled, the mechanism of the reaction being expressible in the form

$$\begin{array}{c} I' \\ {>} Fe^{..} + Fe^{..} {<} \begin{array}{c} I' \\ I' \end{array} + h\nu = \begin{array}{c} I' \\ I' \end{array} {>} Fe^{...} + Fe^{...} {<} \begin{array}{c} I' \\ I' \end{array} + I' : \\ I' \\ I - I' - I \end{array}$$
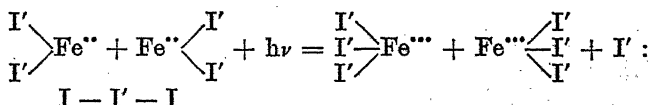
and that the minimum value of a photochemically active quantum corresponded to a wave-length $\lambda = 5790$ Å. or a potential of 2·14 volts.

Further investigation indicated that the photosensitive constituent was the iodine; both the iron salts and the iodine ion being inactive over the region of spectrum employed. The value of the quantum determined in this way, $\lambda = 5790$ Å., $E = 49,200$ cals. per gm.-mol., or $V = 2·14$ volts, agrees very closely with the resonance potential of the iodine molecule, $2·34 \pm 0·2$ volts, as determined by Foote and Mohler (" The Origin of Spectra," p. 78), thus supporting the evidence obtained from this investigation that the photochemical action results from the optical excitation of the iodine, and that the level of energy corresponding to the resonance potential of the iodine molecule is also a chemically active state of excitation.

<center>EXPERIMENTAL.</center>

(a) *Isolation of the Photochemically Active Light of Minimum Quantum Value.*

Equal volumes of two solutions of the compositions, (A) Ferric ammonium alum 0·02 molar, ammonium sulphate 0·02 molar,

made up to $N/10$ by the addition of sulphuric acid, and (B) potassium iodide 0·09 molar, were mixed. The following reaction occurs :

$$Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O + (NH_4)_2SO_4 + 4·5KI + 5H_2SO_4 \rightleftharpoons$$
$$2FeSO_4 + 2(NH_4)_2SO_4 + K_2SO_4 + I_2 + 2·5KI + 5H_2SO_4.$$
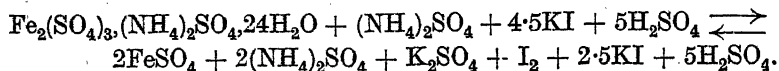
The liberation of iodine proceeds rapidly at the start in the dark, and equilibrium is almost attained at the end of 24 hours, but a slow reaction goes on for several weeks.

As source of light, a 1000 c. p. gas-filled lamp (110 volts, 10 amps.) was employed in conjunction with a series of " M " light filters (Wratten type) for isolating comparatively narrow regions of the spectrum. The cuts of these filters as published by the makers were confirmed by means of a direct-vision spectroscope and found to be accurate under the conditions of the experiment. Both the gelatin light filter and the flat-sided, glass-stoppered reaction vessel were maintained at a uniform temperature of 25° in glass-sided troughs by means of a water-circulating system from a controlled thermostat. In order to obtain approximate equality of intensity in the transmitted light, the distance of the lamp from the filter was changed for each combination of filters according to their transmission as published by the makers.

To follow the change in equilibrium, the amount of iodine in solution was estimated by titration of 5 c.c. of solution run into 100 c.c. of water at 0° with approximately $N/200$-sodium thiosulphate solution, using starch as indicator. The usual precautions concerning the quantity of starch and standardisation of the weak thiosulphate solution were taken. The following results were obtained :—

Filter.	Wave-length in Å. of light transmitted.	Exposure in hours.	Titration value for the unilluminated solution in c.c. less that for illuminated.
A + C	6500—7000	2	0
F	6000—7000	2	0·60
B + E	5000—6300	2	0·80
C	4000—5100	2	0·15
G + H	5100—5500	2	0
D + H	4300—4700	2	0
B + C	4870—5040	2	0
White		1	8·75

The region of the spectrum responsible for the photochemical change appears from these data to lie between $\lambda = 5500$ and 6500 Å.

The quartz mercury vapour lamp emits a group of strong yellow lines at about $\lambda = 5790$ Å., which can be isolated conveniently by means of a colour filter prepared by the Kodak Co. Replacing the 1000 c. p. lamp by a quartz mercury vapour lamp, the following data were obtained, the time of exposure being in all cases 2 hours.

Filter.	Light transmitted in A.	Titration value in c.c. $N/200$-thio.
Nil	Complete spectrum	6·6
E	5790, 5769, 5679 (and red lines)	1·05
C	4916—4078, 4047	0
H	5461, 4916, 4359, 4348, 4339	0
Mercury green 2% yellow	5461	0·20

These results confirm those obtained with the 1000 c. p. electric lamp and show that, in addition to the ultra-violet light, the lines 5790, 5769, 5679 are photochemically active (the red lines, although absorbed by the solution, being very faint, contributed but little, if any, energy to the system). The line $\lambda = 5790$ Å. corresponds to an energy of excitation of 49,200 calories or a potential of $V = 2\cdot14$ volts, a value, as we have seen, almost identical with the resonance potential of the iodine molecule.

(b) *The Photochemically Active Constituent.*

As has already been indicated, it would appear from the above experiments that the iodine was the photochemically active constituent. Since we are dealing with a reversible system, any alteration in the equilibrium constant would entail a relative alteration in the velocity coefficients of the two reactions :

(1) $I_2 + 2Fe^{\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot\cdot} + 2I'$ k_1
(2) $2I' + 2Fe^{\cdot\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot} + I_2$ k_2
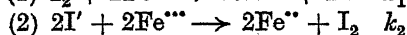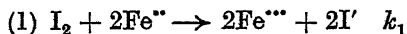
It was accordingly important to find out whether this apparent relative alteration in the velocity coefficients under illumination was produced by the actual alteration in k_1 and that k_2 remained unaltered under illumination.

In order to establish this point a modification of the Harcourt and Esson experiment as used by Donnan and Le Rossignol (J., 1903, **83**, 703) to determine the order of reaction between the ferricyanide and iodide of potassium was employed. Fifty c.c. of the iodide solution B to which 2 c.c. of a standard thiosulphate solution and two drops of starch solution had been added were placed in a vessel provided with a stirrer and maintained at 25° in a thermostat. An equal volume of the ferric iron solution A at 25° was added and the time of appearance of the blue colour noted. Immediately on its appearance, a fresh quantity of thiosulphate solution was added and the time of reappearance of the starch iodine blue observed. With the precautions as to strength of solution and use of the delivery pipette given by Donnan and Le Rossignol, the reaction was carried out at 25° in the dark and in the light of the 1000 c. p. electric lamp. The rates of reaction both in the dark and under illumination were found to be identical.

In the above reaction the iodide-ion concentration was maintained constant during the conversion of the ferric into ferrous ion, and the system is insensitive to illumination. Thus the alteration in the equilibrium of the system under illumination is due to an increase in the velocity of the reaction :—

$$I_2 + 2Fe^{\cdot\cdot} \longrightarrow 2Fe^{\cdot\cdot\cdot} + 2I'.$$
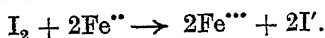
If the increase in the velocity coefficient of this reaction under illumination were due to a photochemical increase in the chemical activity or thermodynamic concentration of the iodine molecules, we should anticipate that a simple concentration cell of the type

Fig. 1.

$$\text{Pt} \qquad\qquad \text{Pt}$$
$$|\quad I_2 \mid KI \mid I_2 \quad|$$
$$\text{in } KI \qquad \text{in } KI$$

Dark.   Illuminated.
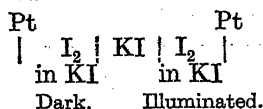
should exhibit a definite electromotive force. Such cells constructed with platinum electrodes and various strengths of iodine solutions in potassium iodide showed after removal of all traces of dissolved oxygen no electromotive force on illumination of one half of the cell. It therefore seems probable that the production of excited iodine molecules by the photochemical action is small compared with the rate at which the reaction $2\epsilon + I_2 \rightleftarrows 2I'$ occurs at the electrode.

(c) *The Application of the Einstein Law of Photoequivalence.*

For the determination of the amount of radiation absorbed and the concomitant chemical action produced by the radiation the following apparatus was employed (Fig. 1) :

A. Mercury vapour lamp. B. Screen. C. Cooling trough. D. Blackened metal plate carrying gelatin light filter, E. F. Cooling trough containing glass-stoppered reaction vessel, G. H. Moll thermopile. I. compensating leads and galvanometer.

The Moll thermopile, H, was first calibrated by means of a Leslie cube, precautions being taken to ensure " black body " radiation as nearly ideal as possible in the circumstances by screening the system of Leslie cube and thermopile with non-conducting material faced with reflecting surfaces in which accurate openings were cut. The radiant energy received by the thermopile from the Leslie cube was calculated by the formula of Lummer and Pringsheim, (*Ann. Physik*, 1897, **63**, 395) and found to be $1\cdot23 \times 10^5$ ergs per sec.
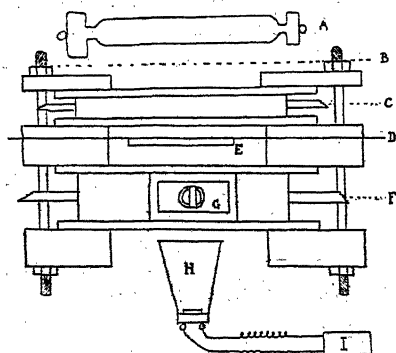
The readings of the galvanometer connected to the thermopile during the radiation fluctuated slightly between 35·4 and 36·4 cm., yielding a mean value of 35·95 cm.

Hence the energy per cm. deflection is $3·423 \times 10^3$ ergs per second. Allowing for the fact that lamp-black surfaces emit and absorb but 90% of the true black-body radiation, the thermopile constant is $2·77 \times 10^3$.

The volume of the solution in G covered by the funnel of the thermopile was found both by measurement and by calculation to be 31 c.c.

The mercury vapour lamp was started and allowed to attain a steady state, the current being checked by means of an ammeter connected in the circuit. The thermopile, suitably protected from draughts, was allowed to come into equilibrium with its surroundings, precautions being taken to keep the room temperature as steady as possible. The bottle was first filled with water and a number of readings were taken of the deflection caused on the galvanometer scale when the screen B was raised. The bottle was then filled up to the mark with the dark equilibrium solution, and a number of readings taken as before.

Since, even with the utmost precaution, mercury vapour lamps are apt to vary in intensity of illumination, a number of independent experiments were performed, of which the two appended represent the extremes of variation. The curve of the rate of disappearance of iodine under the same conditions was also obtained, by means of a large number of experiments which agreed fairly closely.

Water.

	Deflection on galvanometer scale in cm.		Total deflection in cm.	
	Initial.	Final.		
(I)	7·3	27·8	20·5	
	7·2	27·5	20·3	Mean = 20·37
	7·0	27·5	20·5	
	7·0	27·2	20·2	
(II)	5·4	27·8	22·4	
	5·6	28·2	22·6	Mean = 22·53
	5·6	28·2	22·6	

Dark equilibrium mixture.

(I)	6·9	15·1	8·2	
	7·0	15·0	8·0	Mean = 8·1
	6·9	14·8	7·9	
	7·0	15·3	8·3	
(II)	5·4	13·7	8·3	
	5·6	14·2	8·6	Mean =
	5·4	14·0	8·6	

Energy absorbed by solution in (I) = 12·3 × 2·
Energy absorbed by solution in (II) = 14·
Mean =

The rate of disappearance of iodine under the same conditions was next investigated.

At various times, $5 \cdot 15$ c.c. were withdrawn, run into 100 c.c. of cold water, and titrated with approx. $N/100$-thiosulphate, the following data being obtained from which the velocity coefficient $[k = 1/t.\log a/(a - x)]$ has been calculated : $a = 7 \cdot 5 \times 0 \cdot 0012696$ g. of I_2.

T (mins.).	$N/100$-Thio. (c.c.).	t.	x.	k.
0	7·50	15	0·0006345	0·00463
15	7·14	30	0·001142	0·00430
52	6·20	60	0·002030	0·00404
120	5·40	90	0·003173	0·00455
192	4·97			
422	4·91			Mean $= 0 \cdot 00438$

The reaction appears to follow the unimolecular law as indicated by the values of k, hence the initial rate of disappearance of iodine may be calculated.

$$dx/dt = kc = 0 \cdot 00438 \times 0 \cdot 000005 \times 7 \cdot 5 \times 6 \cdot 06 \times 10^{23}$$
$$\text{molecules } I_2 \text{ per minute for } 5 \cdot 15 \text{ c.c.}$$
$$= \underline{0 \cdot 996 \times 10^{16} \text{ molecules } I_2 \text{ per sec. for } 31 \text{ c.c.}}$$

We can now proceed to calculate the number of quanta absorbed per sec. by the solution.

Wave-length $= 5790 \cdot 66$ Å.   Frequency $\nu = 5 \cdot 176 \times 10^{14}$.
Magnitude of quantum $= h\nu = 6 \cdot 55 \times 10^{-27} \times 5 \cdot 176 \times 10^{14}$
$$= 3 \cdot 39 \times 10^{-12} \text{ erg.}$$

Energy absorbed by solution $= 13 \cdot 2 \times 2 \cdot 77 \times 10^3$ ergs per sec.
Hence number of quanta absorbed by solution
$$= \underline{1 \cdot 078 \times 10^{16} \text{ per sec.}}$$

There are thus $0 \cdot 996 \times 10^{16}$ molecules of iodine being decomposed per second by $1 \cdot 078 \times 10^{16}$ quanta. The reaction thus obeys the Einstein law of photochemical equivalence under the conditions of the experiment.

(d) The Temperature Coefficient of the Reactions.

The influence of temperature on the dark equilibrium system

$$2Fe\cdot\cdot + I_2 \underset{\longleftarrow}{\overset{\longrightarrow}{}} 2Fe\cdot\cdot\cdot + 2I'$$
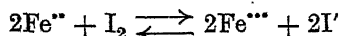
is negligibly small, but the rate at which equilibrium is attained
dependent on the temperature; this rate was investigated
and the equilibrium point was reached in each
the warmer solutions.   By estimation
. after mixing the solutions A and B

at the two temperatures, the temperature coefficient was calculated from the velocity coefficients to be, for a rise in temperature of 10°, $k_{35°}/k_{25°} = 2·713$. The influence of temperature on the rate of attainment of the light equilibrium was investigated by a potentiometric method. A photovoltaic cell consisting of bright platinum electrodes inserted in a constricted ∪-tube containing the dark equilibrium mixture was employed. On illumination of one limb of the ∪-tube with monochromatic yellow radiation at 25°, the equilibrium concentration in the exposed limb is altered and the rate of alteration can be determined from the electromotive force of the cell. On cutting off the radiation, the return of the photochemical equilibrium mixture to the dark equilibrium can readily be followed from the electromotive force of the cell. As typical of the readings obtained by this method the following values may be cited.

Temperature 25°.				Temperature 35°.			
Time in mins.	Milli-volts.	Time in mins.	Milli-volts.	Time in mins.	Milli-volts.	Time in mins.	Milli-volts.
0	0·0	130	10·30	0	0·0	50	8·60
5	0·9	140	10·30	5	1·40	60	9·25
20	3·05	Light off		10	2·80	70	9·65
40	5·90	142	10·20	20	4·85	80	10·00
60	7·95	145	9·70	30	6·40	90	10·17
75	8·95	150	8·85	40	7·65	100	10·17
90	9·65	185	6·45				
113	10·05	190	6·25				
		200	5·90				

From the velocity coefficients of the rate of attainment of photochemical equilibrium the temperature coefficient $k_{35°}/k_{25°}$ (light) was found to be 1·17. It is probable that the velocity of the true photochemical reaction is not influenced by temperature and that the value of 1·17 obtained is due to the effect of the increase in velocity of the dark reaction with the temperature superimposed on the velocity of the light reaction.

The Influence of Ionic Activities on the Photochemical Equilibrium.

It has already been noted that although the liberation of iodine from the reacting system commences rapidly, yet the reaction comes but slowly to equilibrium. At the end of 24 hours, the average amount of iodine liberated as determined by titration with thiosulphate was found equivalent to 7·80 c.c. of $N/100$-thiosulphate for 5·15 c.c. of the equilibrium mixture. Although the reaction is apparently completed, nevertheless a slow reaction is still proceeding towards a true equilibrium. This equilibrium was established at the end of 3 months and found equal to 8·37 c.c. of $N/100$-thiosulphate. Since the equilibrium attained is the result of the attainment of equal velocity for two reactions, $2Fe^{··} + I_2 \longrightarrow$

κ*

$2Fe^{\cdots} + 2I'$ and $2Fe^{\cdots} + 2I' \longrightarrow 2Fe^{\cdots} + I_2$, it is clear that if the active masses of equilibrium concentrations of the reactants could be raised in equal proportion the reaction velocities of each reaction would proceed more rapidly and equilibrium would be more rapidly attained.   The active masses or thermodynamic concentrations of the active ions, whether simple as indicated above or complex as imagined by Sasaki (*Z. angew. Chem.*, 1924, **137**, 181), can readily be raised by the addition of a neutral salt such as potassium chloride (Brönsted, *Z. physikal. Chem.*, 1922, **103**, 307).   In the following curves (Fig. 2) the rate of attainment of equilibrium in the dark for three mixtures to which varying amounts of potassium chloride have been added are given.

FIG. 2.

Time, minutes.
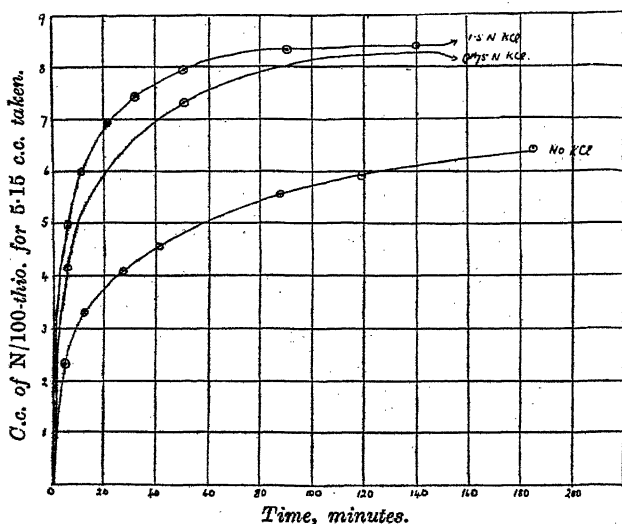
It is clear from the curves that the augmentation in thermo-dynamic concentration of the reacting ions by the addition of the potassium chloride has, as anticipated, augmented the rate at which true equilibrium is attained.   That the separate reaction velocities are in reality augmented by the addition of potassium chloride was confirmed by repeating the modified Harcourt and Esson experiment as already described in presence of $1.5N$-potassium chloride and in the ordinary solution without the salt addition.   The marked increase in the velocity of the forward reaction on the addition of potassium chloride is evident from the following data :

Time in minutes for appearance of starch-iodide colour.

Thio added (c.c.)	1	2	3	4	5	6	7	8	9
No KCl added	0·5	0·8	1·5	2·8	4·7	8·15	13·7	25·0	
In 1·5N-KCl .	0·4	0·6	1·0	1·6	2·4	3·6	5·6	8·9	16·6

At equilibrium in the dark the rates of the forward photosensitive reactions are given in absence and presence of potassium chloride by the equations $dx/dt = k \cdot f(I_2)f(Fe^{\cdot\cdot})^2 = a$, and $dx'/dt = k \cdot f'(I_2)f'(Fe^{\cdot\cdot})^2 = b$, where f and f' are the activity coefficients in absence and presence of the neutral salt. On illumination of the solutions the respective velocities become

$$dx/dt_{\mathrm{ill.}} = k \cdot f(I_2)f(Fe^{\cdot\cdot})^2 + I(I_2) = a + x,$$
$$dx'/dt_{\mathrm{ill.}} = k \cdot f'(I_2)f(Fe^{\cdot\cdot})^2 + I(I_2) = b + x,$$

where I is the intensity of the photoactive radiation.

The ratio of the velocities of the two dark and light reactions without and in presence of salt will evidently be,

Without KCl present, $V_{\mathrm{ill.}}/V_{\mathrm{dark}} = (a + x)/a = 1 + x/a.$
With KCl present, $V_{\mathrm{ill.}}/V_{\mathrm{dark}} = (b + x)/b = 1 + x/b.$

Thus, the greater the absolute velocity of the forward reaction at equilibrium the smaller will be the apparent effect of the light on the equilibrium. We should thus anticipate that the shift in the equilibrium obtained with the solution containing potassium chloride on exposure to light will be far less than the shift in the equilibrium of the solution in the absence of potassium chloride on exposure to identical radiation, since the addition of salt has, as has been indicated by the previous experiments, raised the value of f' considerably above f, or $b > a$. These expectations were fully realised by determining the rate of change of the dark equilibrium mixture on illumination both by the potentiometric method and by titration. The following data were obtained for a dark equilibrium mixture containing $1 \cdot 5N$-potassium chloride exposed to monochromatic radiation at $25°$.

Time (mins.).	Milli-volts.	$N/100$-Thio. (c.c.).	Time (mins.).	Milli-volts.	$N/100$-Thio. (c.c.).
0	0	7·86	41	2·40	—
1	0·1	—	52	2·60	—
8	0·8	—	60	2·65	7·30
10	1·05	—	70	2·70	—
25	1·90	—	170	2·70	7·30
30	2·15	7·75			

The final value of 2·70 mv. as compared with a value of 10·3 mv. for the solution in the absence of potassium chloride (see Table, p. 265) and a shift in the equilibrium concentration of iodine equivalent to only 0·56 c.c. of $N/100$-thiosulphate solution as compared with the value 2·50 c.c. obtained without the potassium chloride, indicated clearly the effect of augmenting the velocity of the two reactions proceeding in either direction at equilibrium by elevation of the thermodynamic concentrations of the reactants.

The value of the equilibrium constant for the reaction

$$K = (Fe^{..})(I_2)^{\frac{1}{2}}/(Fe^{...})(I')$$

has been determined by Maitland (Z. Elektrochem., 1906, **112**, 263) and by Brönsted and Pedersen (Z. physikal. Chem., 1922, **103**, 307). Maitland obtained the value $K = 10^{2 \cdot 005}$, whilst the data of Brönsted and Pedersen yielded a value of $K_{25°} = 21 \cdot 1$, utilising a value of $L_{25°} = 0 \cdot 00611$ for the equilibrium constant

$$L = (I')(I_2)/(I'_3) = 0 \cdot 0061.$$

The data obtained in the above experiments permit us to calculate the value of K.

The original concentration of ferric ions = 0·02 gm.-atom per litre.
    ,,   ,,   ,,   of iodide ions = 0·045 gm.-atom per litre.

The titre of the dark equilibrium solution is 8·37 c.c. of N/100-thiosulphate for 5·15 c.c.   Hence at equilibrium we obtain :

$(Fe^{...}) = (2 \cdot 0 - 8 \cdot 37/5 \cdot 15)10^{-2}$ gm.-atom per litre.
$(Fe^{..}) = 8 \cdot 37/5 \cdot 15.10^{-2}$ gm.-atom per litre.
$(I') = 8 \cdot 37/5 \cdot 15.10^{-2}$ gm.-atom per litre.

Also, if the original iodide concentration be x and the final $x - a$, we obtain

$I_3' = 3a$
$I' = x - a$ and $(x - 2a)(x - a)/3a = 0 \cdot 00611$ . . . . . (I).
$I_2 = x - 2a,$

where $x = (4 \cdot 5 - 8 \cdot 37/5 \cdot 15)10^{-2}$ gm.-atom per litre
        $= 2 \cdot 875 \times 10^{-2}$ gm.-atom per litre.

Inserting this value of x in (I) and solving for a, we obtain

$a = 0 \cdot 58 \times 10^{-2}$ gm.-atom per litre.

Hence $(I') = \{2 \cdot 875 - 0 \cdot 58\} \times 10^{-2} = 2 \cdot 30 \times 10^{-2}$ gm.-atom per litre.

Hence $K_{25°} = \dfrac{(1 \cdot 625 \times 10^{-2})(1 \cdot 625 \times 10^{-2})^{\frac{1}{2}}}{(0 \cdot 380 \times 10^{-2})(2 \cdot 30 \times 10^{-2})} = 23 \cdot 6,$

a value in close agreement with that of Brönsted and Pedersen.

The slight discrepancy between 23·6 and 21·1 for the values of K in the two investigations is probably accounted for by the fact that Brönsted and Pedersen utilised only chlorides and iodides of iron and potassium whilst in the present case ammonium sulphate was present in addition.

Summary.

The reaction $2Fe^{...} + I_2 \rightleftarrows 2Fe^{..} + 2I'$ is photosensitive to both ultra-violet and visible light. The region of visible photoactive radiation is within the range 5500—6500 Å. with an apparent

maximum at 5800 Å. The tri-iodide ion is the photoactive constituent, and the energy of excitation corresponding to a wavelength 5800 Å. is equivalent to 2·14 volts, a value almost identical with the resonance potential of the iodine molecule. It is found that one quantum of absorbed radiant energy causes 1 mol. of iodine to react; the mechanism of the reaction can be expressed in the form $2\overbrace{FeI_2 + I_3'} + h\nu = 2FeI_3 + I'$.

The dark equilibrium constant of the reaction is

$$K = 23\cdot6 = (Fe^{\cdots})(I_2)^{\frac{1}{2}}/(Fe^{\cdots})(I') \text{ at } 25°.$$

The temperature coefficient of the liberation of iodine in the dark is $k_{35°}/k_{25°} = 2\cdot713$, whilst that of the photochemical reaction is $k'_{35°}/k'_{25°} = 1\cdot17$. The addition of potassium chloride raises the thermodynamic concentrations of all the reactants and, although the equilibrium point is unchanged, the rate of attainment is very considerably increased.

Proof is given that equilibrium is the result of attainment of equal velocities of the forward and the back reaction, since the effect of radiation of constant intensity on the equilibrium attained is less when the thermodynamic concentrations of the reactants (and thus the reaction velocities of the two reactions) are raised by the addition of potassium chloride.

XLIV.—The Condensation of Phenylethylamine with s-Dichlorodimethyl Ether.

By WALLACE FRANK SHORT.

BY the action of β-phenylethylamine on an excess of methylal in presence of concentrated hydrochloric acid at 100°, Pictet and Spengler (*Ber.*, 1911, 44, 2030) obtained tetrahydro*iso*quinoline in 36% yield. By a similar method, Pictet and Gams (*Ber.*, 1911, 44, 2629) prepared hydronorhydrastinine from homopiperonylamine, but Decker and Becker (*Ber.*, 1912, 45, 2404), who repeated the experiments, obtained a base of the type $NHR\cdot CH_2\cdot NHR$. Phenylethylamine itself yielded β-phenylethyldimethylamine when condensed with an excess of formalin at 130—140°. The same

authors have shown (*Annalen*, 1913, **395**, 342) that homopiperonyl-amine and other derivatives of β-phenylethylamine react readily at room temperature with an equimolecular quantity of an aldehyde to form the alkylidene derivative, which is converted into a tetra-hydro*iso*quinoline derivative by a suitable catalyst.

Rosenmund (*Ber. Deut. pharm. Ges.*, 1919, **29**, 200) condensed homopiperonylamine (2 mols.) with *s*-dichlorodimethyl ether (1 mol.) in ethereal solution and obtained homopiperonylaminomethanol as a very unstable oil, which was converted almost quantitatively into hydronorhydrastinine by heating at 100° with 10% hydrochloric acid.

In view of the above results, it appeared to be of interest to determine whether a good yield of tetrahydro*iso*quinoline could be obtained by the condensation of β-phenylethylamine with the so-called "chloromethyl alcohol." The products of the reaction were tetrahydro*iso*quinoline (yield 59%), *di*(β-*phenylethylamino*)-*methane*, and bases of unknown constitution.

<div align="center">EXPERIMENTAL.</div>

β-Phenylethylamine was obtained in 30% yield (Wohl and Berthold, *Ber.*, 1910, **43**, 2183). *s*-Dichlorodimethyl ether was prepared by Stephen, Short, and Gladding's method (J., 1920, **117**, 513).

A mixture of 31·5 g. (2 mols.) of β-phenylethylamine hydro-chloride, 14·4 g. of *s*-dichlorodimethyl ether (1¼ mols., equivalent to 2½ mols. of chloromethyl alcohol), 0·5 g. of anhydrous zinc chloride, and 100 c.c. of dry ether was cooled to room temperature, stirred for ½ hour, and heated for 4 hours on the water-bath. Dis-tillation in a vacuum left a brown syrup, which was dissolved in water, the solution made alkaline, and extracted with ether. The oily residue from the ethereal extract on solution in dilute hydro-chloric acid and treatment with sodium nitrite gave a yellow oil, which, on reduction with tin and concentrated hydrochloric acid, deposited β-phenylethyl chloride. The aqueous layer was extracted with ether, made alkaline with caustic soda, and again extracted with ether. The second extract was distilled up to 235°, and the distillate converted into a picrate which, crystallised thrice from alcohol, melted at 196°; the base generated therefrom by addition of ammonia had b. p. 234°/763 mm. (yield 15·7 g.) (Found : C = 81·10; H = 8·39. Calc. for $C_9H_{11}N$, C = 81·15; H = 8·33%). These constants are in good agreement with those given in the literature for tetrahydro*iso*quinoline, and show that the product cannot be Becker and Decker's β-phenylethyldimethylamine.

The residue in the distilling flask was dissolved in hydrochloric acid, boiled with animal charcoal, and recrystallised several times

from water. The colourless crystals so obtained did not melt at 300°. The base, liberated with caustic soda, consisted of white needles of *di*(β-*phenylethylamino*)*methane*, m. p. 153°, and absorbed carbon dioxide from the air (Found : C = 80·16; H = 8·73; N = 10·82. $C_{17}H_{22}N_2$ requires C = 80·25; H = 8·72; N = 11·02%). About 10% of the β-phenylethylamine is converted into this secondary diamine. The *diacetyl* derivative forms silky needles, m. p. 191°.

My thanks are due to Mr. F. H. V. Fielder, B.Sc., for assistance in preparing the β-phenylethylamine for this investigation.

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XLV.—*New Halogen Derivatives of Camphor. Part VI. β-Bromocamphor-α-sulphonic Acid. Part VII. The Constitution of the Reychler Series of Camphorsulphonic Acids. Experiments on Chlorosulphoxides.*

By HENRY BURGESS and THOMAS MARTIN LOWRY.

Part VI.—β-*Bromocamphor-α-sulphonic Acid.*

THE present paper describes a new series of sulphonic derivatives of camphor, in which the sulphonic group occupies the α-position. This result is of interest, since sulphonation has hitherto always been found to result in an attack upon a methyl group, whilst the very reactive α-carbon atom has escaped. Thus even the gentle method of sulphonation used by Reychler gives β-derivatives and not the α-sulphonic acid, which he thought he had prepared; and it is only after blocking the β-position with a halogen that we have been able to induce the sulphonic radical to enter the α-position.

Armstrong and Lowry (J., 1902, **81**, 1445) had already attempted to sulphonate β-bromocamphor, but had obtained only a negative result. Our experiments have shown that, although most of the β-bromocamphor can be recovered unchanged, about 15 to 20% of it is sulphonated at each operation. The product was at first thought to be a β-bromocamphor-ρ-sulphonic acid, where ρ represents the position of the sulphonic group in Reychler's acid, but doubts arose when it was found that the sulphonamide did not yield an anhydramide, like α-bromocamphor-ρ-sulphonamide, but gave an acetyl derivative like α-bromocamphor-π-sulphonamide. Still more striking was the fact that the sulphonyl bromide, when

decomposed by heat, did not give a new $\beta\rho$-dibromocamphor, but a mixture of Kachler and Spitzer's $\alpha\beta$-dibromocamphor with our new $\alpha'\beta$-dibromocamphor (J., 1923, **123**, 1867). This suggested that the sulphonic group occupied the α-position; but as the whole research was based upon a suspicion that the pyrogenic decomposition of a ρ-sulphonyl bromide might give a β-bromo-compound of different orientation, we did not regard it as safe to accept the above observation as a final proof of the structure of the acid. Confirmation was, however, obtained when the sulphonamide on bromination again gave rise to the same $\alpha\beta$-dibromocamphor, by a remarkable action in which *the halogen displaces a sulphonamide group* instead of eliminating one of the reactive α-hydrogen atoms. This result was very difficult to explain unless the sulphonic group were already in the α-position. Moreover, this bromination was free from the suspicions which attached to the formation of $\alpha\beta$-dibromocamphor by the pyrogenic decomposition of the sulphonyl bromide. Final proof that the sulphonic group had entered the α-position, leaving the camphor nucleus intact except for the presence of the β-bromine atom, was obtained when the spontaneous oxidation of a dibromosulphonamide derived from our acid gave rise to the hitherto unknown β-*bromocamphorquinone*, and thence by a direct further oxidation to β-*bromocamphoric anhydride* (not the free acid, although the oxidation took place in aqueous solution).

The whole series of actions may be set out as follows :

(I.) $C_8H_{13}Br\begin{smallmatrix}CH\cdot SO_2\cdot OH\\CO\end{smallmatrix}$ $\xrightarrow{PBr_5}$ $C_8H_{13}Br\begin{smallmatrix}CH\cdot SO_2Br\\CO\end{smallmatrix}$ (II.)

β-Bromocamphor- β-Bromocamphor-
a-sulphonic acid.   a-sulphonyl bromide.

(III.) $C_8H_{13}Br\begin{smallmatrix}CH\cdot SO_2\cdot NH_2\\CO\end{smallmatrix}$ $\xrightarrow{Br_2}$ $C_8H_{13}Br\begin{smallmatrix}CHBr\\CO\end{smallmatrix}$

β-Bromocamphor- $\alpha\beta$-Dibromocamphor.
a-sulphonamide.

(IV.) $C_8H_{13}Br\begin{smallmatrix}C\cdot SO_2\cdot NH_2\\C\cdot O\cdot CO\cdot CH_3\end{smallmatrix}$ $\xrightarrow{Br_2}$ $C_8H_{13}Br\begin{smallmatrix}CBr\cdot SO_2\cdot NH_2\\CO\end{smallmatrix}$ (V.)

Acetyl $\alpha'\beta$-Dibromocamphor-
derivative.   a-sulphonamide.

$C_8H_{13}Br\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}O$ $\xleftarrow{O_2}$ $C_8H_{13}Br\begin{smallmatrix}CO\\CO\end{smallmatrix}$ (VI.)

β-Bromocamphoric β-Bromocamphorquinone.
anhydride.

In these formulæ the acetyl derivative has been assumed to be enolic, as in the case of the π-isomeride, the solubility of which (unlike that of the amide from which it is derived) is not increased by the addition of alkali (Lowry and Magson, J., 1906, **89**, 1044), so that the acetyl derivative appears not to contain an α-hydrogen atom.   In the present case, the fact that the acetyl group was lost on bromination suggested very strongly that we were again dealing with an enolic acetate and not the –SO_2·NHAc compound.

This investigation confirms the view of Lipp and Lausberg (*Annalen*, 1924, **436**, 274) that β-*bromocamphor and the Reychler series of camphorsulphonic acids have the same orientation,* since the blocking of the β-position by a halogen compels the sulphonic group to enter a new position in the molecule.   The question whether the β-substituents are attached to a carbon atom in the ring, or to a methyl group is discussed in Part VII below.

Experimental.

Sulphonation of β-*Bromocamphor.*—β-Bromocamphor (50 g.) was added slowly to a mixture of acetic anhydride (80 c.c.) and concentrated sulphuric acid (25 c.c.), when the mixture became brown and most of the β-bromocamphor dissolved.   After standing for a week at 30—40°, it was heated for 2 hours and poured on to crushed ice, and the precipitated β-bromocamphor (41 g.) washed with water.   Further heating, or varying the quantities of acetic anhydride and sulphuric acid, gave a smaller yield of sulphonate and a much larger quantity of brown charred material.   The solution was boiled till free from acetic acid, neutralised with a cream of calcium carbonate, filtered, and concentrated.   The sludge of chalk and calcium sulphate (which separates only slowly in the presence of the calcium sulphonate) was washed three times with boiling water to remove all the sulphonate.   After recrystallising three times from methylated spirit, the calcium sulphonate was obtained in colourless, rhombic plates.   The mother-liquors were decolorised by bone charcoal.   The total yield was 12 g. (about 90%) after allowing for the recovery of most of the bromocamphor.   0·1515 gave 0·1800 of CO_2, 0·0660 of H_2O, and 0·0273 of $CaSO_4$.   0·1773 lost 0·0172 of H_2O, and gave 0·0924 of AgBr :   C = 32·41, H = 4·87, Ca = 5·30, Br = 22·18, H_2O = 9·70. $(C_{10}H_{14}OBr·SO_3)_2Ca,4H_2O$ requires C = 32·78, H = 4·95, Ca = 5·47, Br = 21·83, H_2O = 9·84%.

Calcium β-*bromocamphor-α-sulphonate* is very soluble in hot water, but crystallises readily from hot methylated spirit.   It does not melt below 250°.   It has $[α]_{5780} = + 50°$, $[α]_{5461} = + 59°$, $[α]_{4358} = + 116·5°$ in water (2 g. per 100 c.c.).

Potassium β-*bromocamphor-α-sulphonate*, prepared by addition of potassium oxalate (calc. amt.) to a solution of the calcium salt, filtration, and evaporation, crystallised from hot methyl alcohol in fine, colourless needles. 0·2045 gave 0·2565 of CO_2 and 0·0730 of H_2O. 0·2152 lost no water at 150—160° in a vacuum : C = 34·22, H = 4·00. $C_{10}H_{14}OBr \cdot SO_3K$ requires C = 34·37, H = 4·04%.

β-*Bromocamphor-α-sulphonyl Chloride* (Formula as II).—A mixture of powdered phosphorus pentachloride (5·4 g.) and the dry, powdered potassium salt (7·5 g.) was shaken and warmed in a dry flask on the water-bath, until liquid. After 15 minutes, it was shaken vigorously with powdered ice. The light brown solid was filtered, and washed with water and a little dilute potassium carbonate solution; it crystallised from ether in large, compact crystals (Fig. 1), which softened at 93° and melted at 97°. 0·2393
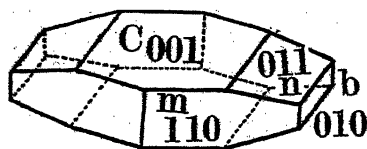
FIG. 1.   FIG. 2.
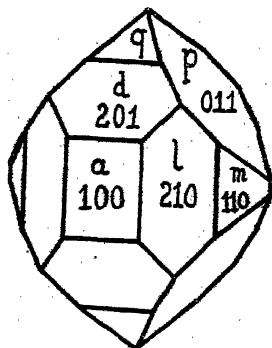
gave 0·0940 of AgCl : Cl = 9·7. $C_{10}H_{14}OBr \cdot SO_2Cl$ requires Cl = 10·76%.

β-Bromocamphor-α-sulphonyl chloride is comparatively stable when pure, but loses chlorine quickly if impure, and especially in presence of a little hydrochloric acid. It is very soluble in benzene or ether, less soluble in cold alcohol, and sparingly soluble in light petroleum.

The crystallographic properties are as follows (two crystals were measured) :

System : Orthorhombic.

Axial Ratios : $a : b : c = 0·2994 : 1 : 0·3769$.

Habit : Both crystals were flattened parallel to $C(001)$, with $m(110)$ fairly large. The crystals were not quite transparent, and did not give good reflections.

Forms present : $C(001)$, $b(010)$, $m(110)$, and $n(011)$. One face only of $y(021)$.

Angles observed.	No. of measurements.	Limits.	Mean observation.	Calculation.
bm 010 : 110	8	69° 52′ —68° 59′	69° 21′	—
cn 001 : 011	8	17 1½—16 30	16 40	—
cy 001 : 021	1	30 25½—31 35½	31 0½	30° 55′
mn 110 : 011	4	84 28 —84 2	84 11	84 12

Optical Characters : Since the crystals could not be immersed in liquids, the optical data are scanty, and liable to be inaccurate. The optic axial plane is parallel to $b(010)$, with the acute bisectrix perpendicular to $C(001)$, and the double refraction positive. The refractive indices determined by the minimum deviation method are very approximately $\alpha = 1·55$, $\beta = 1·56$, $\gamma = 1·58$.

β-*Bromocamphor-α-sulphonamide* (Formula III).—A mixture of the potassium sulphonate (7·0 g.) and phosphorus pentachloride (4·2 g.) was covered with dry chloroform (50 c.c.) and left overnight. The chloroform was washed twice with ice-cold water, dried for an hour over calcium chloride, filtered, and excess of dry ammonia was passed into it, when much heat was developed. After 12 hours, the chloroform was distilled off, and the residue was washed with water and crystallised from ether (yield 65%). 0·2045 gave 0·2895 of CO_2 and 0·0955 of H_2O. 0·2268 gave 0·1382 of AgBr: C = 38·62, H = 5·23, Br = 25·93. $C_{10}H_{16}O_3NBrS$ requires C = 38·71, H = 5·20, Br = 25·77%.

β-Bromocamphor-α-sulphonamide is very soluble in chloroform, alcohol, ether, or hot benzene, less soluble in cold benzene, and sparingly soluble in light petroleum or water. It melts at 100— 102°, with the evolution of small bubbles of gas, and has $[\alpha]_{5780}$ + 39·3°, $[\alpha]_{5461}$ + 46·1°, $[\alpha]_{4358}$ + 99° in alcohol (5·62 g. per 100 c.c.).

The crystals which separate from an ethereal solution are tough and fibrous when crushed, they are at first quite transparent, but after about 2 hours the surface becomes opaque, and then the whole of the crystal, perhaps as a result of polymorphic change. When this change is complete, the crystal is easily crushed, the fibrous structure having been lost completely.

Attempts to Prepare an Anhydramide.—Lowry's two methods (J., 1902, **81**, 1441) were employed.

(a) A mixture of the sulphonamide (0·5 g.) with 45 c.c. of concentrated hydrochloric acid was kept for a fortnight, the clear solution diluted with water (2 vols.), and neutralised with potassium carbonate. Chloroform extracted the sulphonamide unchanged.

(b) The sulphonamide (2·5 g.) was heated with acetic anhydride (10 c.c.) on the water-bath for 4 hours,* crystals separating. After

* If the mixture is boiled, instead of being heated on a water-bath, considerable charring occurs.

cooling, these were filtered off and a further small quantity was obtained by diluting the cold mother-liquor with water (yield 80%). Although this product resembled α-bromocamphor-β-sulphonanhydramide in appearance and in its sparing solubility in all solvents, it was an *acetyl* derivative, for 0·2060 gave 0·3140 of CO_2 and 0·0955 of H_2O, and 0·1900 gave 0·1032 of AgBr and 0·1280 of BaSO$_4$:   C = 41·58,   H = 5·19,   Br = 22·89,   S = 9·25. $C_{10}H_{18}O_4NBrS$ requires C = 40·90, H = 5·15, Br = 22·69, S = 9·10%.

Acetyl-β-bromocamphor-α-sulphonamide (IV), prepared as described above, is slightly soluble in hot acetone, and in hot acetic anhydride, but is sparingly soluble in the cold solvents and in all the other common organic solvents. It crystallises from acetone in small, compact crystals, m. p. 217° (rapid decomp.). It has $[\alpha]_{5780} - 37\cdot5°$, $[\alpha]_{5461} - 42°$ in acetone (0·613 g. per 100 c.c.).

The crystallographic properties are as follows :

System : Orthorhombic.

Axial Ratios : $a : b : c = 1\cdot804 : 1 : 1\cdot206$.

Forms present : a(100), m(110), l(210), q(101), d(201), p(011).

Habit : The crystals were very small (Fig. 2), the longest dimension being about $\frac{1}{5}''$. The faces were frequently curved and not well suited to accurate measurement. The face a(100) was only observed on two crystals. The prism faces were always very small, with the domes predominating, to give a stumpy outline.

Angles observed.	No. of measurements.	Limits.				Average.		Calculated.	
mm' = 110 : $\bar{1}$10	5	57°	29'—	59°	51'	58°	43'	58°	0'
ll' = 210 : 2$\bar{1}$0	5	84	22 —	86	16	85	32	84	6
pp' = 011 : 0$\bar{1}$1	6	99	58 —102		24	101	0	100	40
qq' = 101 : $\bar{1}$01	6	67	54 —	70	23	68	50	67	32
dd' = 201 : 20$\bar{1}$	6	73	0 —	75	19	74	9	73	34
mq = 110 : 101	6	71	22 —	73	49	73	13	74	22
mp = 110 : 011	5	46	53 —	48	31	47	52	47	41
ld = 210 : 201	10	53	51 —	56	19	54	18	53	30
lp = 210 : 011	10	56	34 —	59	25	57	43	58	58
lq = 210 : 101	4	65	13 —	65	41	65	26	65	37
md = 110 : 201	2	66	41 —	68	44	67	24	67	9

Cleavage : None observed.

Specific gravity : 1·562 determined by floating in Thoulet's solution.

Decomposition of β-*Bromocamphor-α-sulphonyl Bromide* (Formula II).—The method of preparation was similar to that used in making the sulphonyl chloride. As the oil obtained on evaporating off the chloroform from the washed and dried solution did not crystallise in a desiccator in 2 days, it was dissolved in dry xylene and refluxed for about $\frac{1}{2}$ hour until the evolution of sulphur dioxide, which

was at first very rapid, had practically ceased. The liquid charred rather badly during the heating. After the xylene had been distilled off in steam, a colourless oil came over and slowly solidified. This was filtered off, and melted at 46—85°. When crystallised from dilute alcohol, it gave three successive crops of crystals. The first fraction, which melted almost constantly at 92—94°, on three successive crystallisations, was at once converted into almost pure αβ-dibromocamphor on crystallising in presence of a trace of piperidine, and therefore was a mixture of αβ- and α'β-dibromocamphors (compare J., 1923, **123**, 1872). The second fraction, after one further crystallisation, was identified as α'β-dibromocamphor (m. p. 133—135°, not lowered by mixing; $[\alpha]_{5461}$ — 77° instead of — 85° in acetone, 1 g. per 100 c.c.). The third fraction was identified, after one further crystallisation, as αβ-dibromocamphor (m. p. 113—114°, not lowered by mixing with αβ-dibromocamphor; $[\alpha]_{5461}$ 125° instead of 127° in acetone, 3·92 g. per 100 c.c.). The above results proved quite conclusively that the sulphonyl bromide had decomposed to a mixture of αβ- and α'β-dibromocamphors.

Bromination of β-Bromocamphor-α-sulphonamide.—Bromine (2·7 g.) was added to a solution of the sulphonamide (2·0 g.) in glacial acetic (50 c.c.), and the mixture refluxed for 4 hours, becoming pale yellow. From the aqueous solution, neutralised with sodium carbonate, ether extracted an oil (about 2 c.c.), containing some lachrymatory substance, probably bromoacetic acid, from which was separated about 0·3 g. of αβ-dibromocamphor, m. p. 112—114° (alone or mixed with this substance).

α'β-Dibromocamphor-α-sulphonamide (Formula V).—Bromine (2·5 g.) was added to the acetyl derivative of β-bromocamphor-α-sulphonamide (0·8 g.) in glacial acetic acid (20 c.c.), and the mixture refluxed for 5 hours, the acetyl derivative dissolving completely, and the bromine disappearing. After cooling, the acetic acid was neutralised with ammonia, the mixture being cooled meanwhile; the white precipitate crystallised from benzene–ligroin in beautiful, colourless prisms, m. p. 145°, softening at 143° (yield 0·7 g., or 80%). 0·2015 gave 0·2310 of CO_2 and 0·0710 of water. 0·1818 gave 0·1751 of AgBr and 0·1070 of $BaSO_4$: C = 31·27, H = 3·94, Br = 40·99, S = 8·08. $C_{10}H_{15}O_3NBr_2S$ requires C = 30·86, H = 3·89, Br = 41·08, S = 8·24%).

α'β-Dibromocamphor-α-sulphonamide is insoluble in water, sparingly soluble in light petroleum, but very soluble in other organic solvents. It has $[\alpha]_{5780}$ — 26°, $[\alpha]_{5461}$ — 29° in benzene (2·64 g. per 100 c.c.). When warmed with aqueous sodium hydroxide, it liberates ammonia.

β-Bromocamphorquinone (Formula VI).—During a crystallisation

of dibromocamphorsulphonamide from dilute alcohol the solution slowly became yellow, and deposited bright yellow crystals as well as the colourless ones of the initial compound. After a week, a large proportion of the colourless crystals had disappeared, whilst the yellow compound had increased in quantity. The mixture was filtered off and sublimed in a vacuum, when bright yellow prisms, m. p. 104—107°, were obtained. These were recrystallised from dilute alcohol and melted at 122° after softening above 115°. 0·04766 gave 0·03655 of AgBr (micro-Carius): Br = 32·63. $C_{10}H_{13}O_2Br$ requires Br = 32·61%.

Attempts to prepare it by hydrolysis with sodium ethoxide and with calcium hydroxide failed; both gave the intense colour of the quinone, but very little could be separated. Oxidation with hydrogen peroxide in aqueous alcoholic solution first gave the intense yellow colour of the quinone; but further heating led to its decomposition, with the formation of β-bromocamphoric anhydride, m. p. about 143° (alone or mixed with a genuine specimen); the rotatory power (+ 7°) also was in harmony with that (+ 5°) of a specimen of the anhydride prepared from β-bromocamphoric acid. The yellow colour also disappears slowly by oxidation when the quinone is left in contact with aqueous alcohol.

β-Bromocamphorquinone is very soluble in benzene, ether, or chloroform, less soluble in alcohol, and insoluble in water. It has a characteristic pleasant odour which is unlike that of camphorquinone. The absorption spectrum in alcoholic solution of a specimen melting at 104—107° gave an absorption band at the same wave-length as that of camphorquinone. The results are given in Table I.

TABLE I.

The Absorption of β-Bromocamphorquinone in Alcohol.

Conc. of solution = 0·0993 g.-mol. per litre. Length of tube = 1 dcm.

λ.	4300.	4400.	4500.	4550.	4600.	4650.	4700.	4750.
log ϵ_1	0·891	1·012	1·127	1·147	1·158	1·160	1·149	1·145
log ϵ_2	1·15	1·32	1·41	1·458	1·460	1·462	1·460	1·457

λ.	4800.	4850.	4900.	5000.	5100.	5200.	5300.
log ϵ_1	1·120	1·010	0·790	0·261	$\bar{1}$·947	$\bar{1}$·735	$\bar{1}$·626
log ϵ_2	1·425	1·365	1·230	0·528	0·085	$\bar{1}$·442	—

ϵ_1 is the extinction coefficient for β-bromocamphorquinone.

ϵ_2 is the extinction coefficient for camphorquinone (Lowry and French, J., 1924, **125**, 1921).

We are indebted to Mr. R. Jeffery of Peterhouse, for the crystallographic measurements, which he obtained under the direction of Mr. A. Hutchinson, F.R.S.

Part VII.—*The Constitution of the Reychler Series of Camphor-sulphonic Acids.   Experiments on Chlorosulphoxides.*

The position occupied by the sulphonic group in Reychler's camphorsulphonic acid, and the related question of the position of the halogen in β-bromocamphor, have recently come up for reconsideration, since Wedekind, Schenk, and Stusser (*Ber.*, 1923, 56, 633) have discovered a series of reactions by which Reychler's acid can be converted into ketopinic acid by the destruction of one of the methyl groups of the original molecule of camphor. The evidence thus supplied that the sulphonic radical has entered a *methyl* group is, however, at variance with the equally definite evidence that the halogen of β-bromocamphor (which can be pre-pared by the thermal decomposition of the sulphonyl bromide of Reychler's acid) has entered a *methylene* group in the ring. Part of this evidence was reviewed by Armstrong and Lowry (*J.*, 1902, 81, 1469), who directed attention to the oxidation of β-bromo-camphor to β-bromocamphoric acid, but were unable to oxidise it further to a tricarboxylic acid, and by M. O. Forster (*J.*, 1902, 81, 265), who directed attention to the ready conversion of β-bromo-camphor into campholenic acid (compare Part V, *J.*, 1924, 125, 2376): but further results have since become available which point in the same direction. Thus not only is campholenonitrile (II) readily formed by the removal of water from camphoroxime (I),

$$
\begin{array}{ccc}
\overset{(4)}{\text{CH}_2}\!\!-\!\!\overset{(4)}{\text{CH}}\!\!-\!\!\text{CH}_2 & & \text{CH}_2\!\!-\!\!\text{CH}\!\!-\!\!\text{CH}_2 \\
\text{(I.)} \quad | \qquad \text{CMe}_2 \quad | & \rightarrow & | \qquad \text{CMe}_2 \quad | \quad + \text{H}_2\text{O} \quad \text{(II.)} \\
\underset{(10)}{\overset{(6)}{\text{CH}_2}}\!\!-\!\!\text{CMe}\!\!-\!\!\text{C:NOH} & & \text{CH}\!\!=\!\!\text{CMe} \;\; \text{C:N}
\end{array}
$$
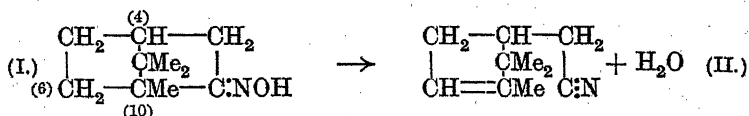
but a similar action takes place in the case of epicamphoroxime, where the methyl group has been transplanted bodily to the 4-position. It is therefore remarkable that this action does not occur in β-bromocamphoroxime, if, as is now suggested, the β-bromine which inhibits the action is in the inactive methyl group, instead of in the methylene group from which the hydrogen of the eliminated molecule of water is taken.

The two lines of evidence disagree so much that it appeared impossible to reconcile them unless (i) a migration of the bromine atom had occurred in the preparation of β-bromocamphor from the sulphonyl bromide of Reychler's acid, or (ii) some change of orientation had taken place during the conversion of the sulphonyl chloride of Reychler's acid into ketopinic acid. The first hypo-thesis is negatived by the results recorded in Part VI above; the present part deals with the second hypothesis.

As a first step in the conversion of Reychler's camphorsulphonyl

chloride to ketopinic acid, Wedekind and his colleagues obtained by loss of water a chlorocamphorsulphoxide which they formulated as follows :

$$
\begin{array}{ccc}
\mathrm{CH_2-CH-CH_2} & & \mathrm{CH_2-CH-CH_2} \\
\mid \quad \mathrm{CMe_2} \mid & \xrightarrow{-H_2O} & \mid \quad \mathrm{CMe_2} \mid \\
\mathrm{CH_2-C-CO} & & \mathrm{CH_2-C-CO} \\
\mathrm{CH_2 \cdot SO_2Cl} & & \mathrm{ClC \vdots S \vdots O}
\end{array}
$$

Reychler's camphor-   10-Chlorocamphor-
sulphonyl chloride.   sulphoxide.
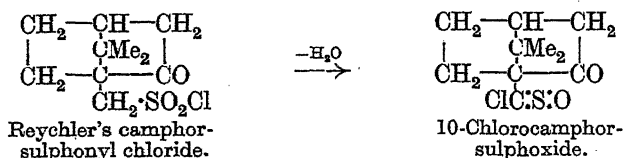
Since they obtained a similar compound from camphor-π-sulphonyl chloride, but not from aromatic sulphonylchlorides, they concluded that *chlorosulphoxides can be obtained only from acids in which a methyl group has been sulphonated.* An alternative view, which would explain the formation of 10-ketopinic acid from a 6-derivative of camphor, postulates instead that a *methyl group must be contiguous to the sulphonic radical,* thus :

$$
\begin{array}{ccccc}
\mathrm{CH_2-CH-CH_2} & & \mathrm{CH_2-CH-CH_2} & & \mathrm{CH_2-CH-CH_2} \\
\mid \quad \mathrm{CMe_2} \mid & \xrightarrow{-H_2O} & \mid \quad \mathrm{CMe_2} \mid & \rightarrow & \mid \quad \mathrm{CMe_2} \mid \\
\mathrm{CH-C-CO} & & \mathrm{CH-C-CO} & & \mathrm{CH_2-C-CO} \\
\mathrm{O{=}S{=}\overline{|O\,H_2|}CH} & & \mathrm{O{=}S{=}C\,(H)} & & \mathrm{O{=}S{=}CCl} \\
\mathrm{Cl} & & (\mathrm{Cl}) & &
\end{array}
$$

Camphor-6-sulphonyl   Camphor-10-chloro-
chloride.   sulphoxide.
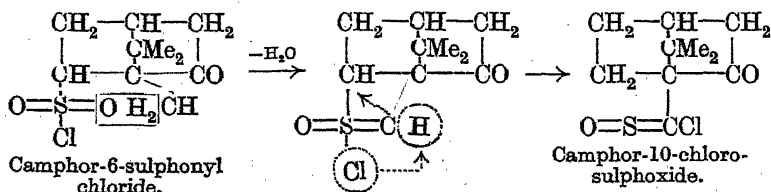
This mechanism assumes that the dehydration of the sulphonyl-chloride involves the formation of an intermediate ring-compound, and the migration of a hydrogen atom from the 10 to the 6-position in addition to the migration of chlorine from sulphur to carbon which was postulated by Wedekind, Schenk, and Stusser.

This mechanism appeared all the more plausible because in camphor-π-sulphonyl chloride there is a methyl group in a precisely similar position relative to the sulphonic radical, since both compounds contain the group $>\!\!\begin{array}{l}\mathrm{C \cdot SO_2Cl} \\ \mathrm{C \cdot CH_3}\end{array}$. In the case of the π-compound, however, it was possible to determine whether a change of orientation had occurred in the dehydration of the sulphonyl chloride, since a different methyl group would then be destroyed on converting into a carboxylic acid (i) the π-bromocamphor obtained by the pyrogenic decomposition of camphor-π-sulphonyl bromide (presumably without change of orientation, compare Part VI above); (ii) the π-chlorosulphoxide obtained by dehydration of the π-sulphonyl chloride by Wedekind's method. If this wandering took place, therefore, the tricarboxylic acid obtained by oxidising Wedekind's *iso*ketopinic acid should be isomeric and not identical

with the acid which Kipping and Pope obtained by hydrolysing and then oxidising π-bromocamphor.

Since Wedekind and his collaborators did not mention whether they had oxidised their product to a tricarboxylic acid, we decided to test the reaction by preparing and oxidising (instead of their compound) an α-bromocamphor-π-chlorosulphoxide prepared from ammonium α-bromocamphor-π-sulphonate. When this was oxidised with nitric acid, a tricarboxylic acid and anhydride were obtained, which were identical and not isomeric with those prepared by Kipping and Pope. There was therefore no evidence here of a change of orientation.

We also attempted to prepare chlorotoluenesulphoxide from o-toluenesulphonyl chloride, since this compound also contains a methyl group in the appropriate position; but we were again unsuccessful, as most of the sulphonyl chloride was recovered unchanged. The evidence therefore undoubtedly proves that the suggested mechanism, which appeared to offer a feasible explanation of the production of 10-ketopinic acid from a camphor-6-sulphonic acid, is incorrect.

We have, then, no alternative but to accept the conclusion that the halogen in β-bromocamphor, as well as the sulphonic group in Reychler's acid, has entered a methyl group and occupies the 10-position in the camphor molecule. In doing so, however, it is desirable to point out that *there is no single reaction in which β-bromocamphor behaves as if it contains the group* $-CH_2Br$. Thus it has never been converted into a primary alcohol, $-CH_2Br \longrightarrow -CH_2 \cdot OH$, and when attempts are made to bring about this change (see Part V), the molecule emerges (as a derivative of campholenic acid) with all its methyl groups intact, but with a double bond in the ring. On the other hand, it is amazing that a halogen in the side chain should absolutely inhibit the formation of this double bond in the ring, when the attempt is made to convert β-bromocamphoroxime into β-bromocampholenonitrile, especially in view of the fact that the side chain can be eliminated completely without affecting the action. The conclusion appears inevitable that there must be some link between the 6- and 10-positions which is not indicated by the conventional formulæ, just as there must be some connexion between the ketonic and the *gem*-dimethyl group (or some mechanism which involves both groups; see Armstrong and Lowry, J., 1902, **81**, 1409) to account for the π-sulphonation of camphor. The nature of this connexion is not yet clear, but it would be shirking the facts not to recognise that there is still a problem to solve, even when the admission has been made that the β-series of compounds are all 10-derivatives of camphor.

EXPERIMENTAL.

α-*Bromocamphor-π-chlorosulphoxide*, $C_9H_{12}BrO\cdot CCl\colon S\colon O$, was prepared by the method of Wedekind, Schenk, and Stusser (*loc. cit.*) from α-bromocamphor-π-sulphonyl chloride, using dry pyridine as the dehydrating agent; but twice as much pyridine was used because the reaction mixture went solid before the addition of the sulphonyl chloride was complete and the later portions did not then react. The brownish-red, granular solid was washed, and crystallised three times from acetone. 0·2003 gave 0·2830 of CO_2 and 0·0700 of H_2O. 0·1930 gave 0·2044 of AgCl + AgBr : C = 38·55, H = 3·91, Br = 25·56, Cl = 11·34. $C_{10}H_{12}O_2ClBrS$ requires C = 38·53, H = 3·88, Br = 25·65, Cl = 11·38%.

α-Bromocamphor-π-chlorosulphoxide is very soluble in benzene, hot acetone, or chloroform, less soluble in cold acetone and the alcohols, slightly soluble in hot ligroin or ether, and insoluble in water. It crystallises in thin plates which are usually pointed at one end, but are occasionally hexagonal in shape. Its colour varies from pale to deep reddish-brown according to the state of aggregation. It melts at 158—159° and has $[\alpha]_{5780} + 31°$, $[\alpha]_{5461} + 39°$ in benzene (5·5 g. per 100 c.c.).

Oxidation of α-Bromocamphor-π-chlorosulphoxide.—This compound (3·5 g.) was refluxed with 20 c.c. of nitric acid (d 1·4) for 14 hours; the mixture was then cooled, and water was added. After extraction with benzene to remove an oily by-product, the aqueous layer was evaporated until crystals began to separate, and then cooled. The crystals, m. p. 180—185°, after filtration and washing with a little water, crystallised twice from benzene–chloroform and once from ether, gave a product which softened slightly at 193° and melted at 194—195° (decomp.); on mixture with a specimen of *trans*-camphotricarboxylic acid supplied by Prof. F. S. Kipping, F.R.S., its m.p. was undepressed. The substance had solubilities similar to those given by Kipping and Pope (J., 1896, **69**, 951) for that acid, and gave precipitates with barium chloride, copper acetate, ferric chloride, and lead acetate as recorded by these authors. It has $[\alpha]_D + 34°$, $[\alpha]_{5780} + 35°$, and $[\alpha]_{5461} + 40°$ in alcohol (0·281 g. in 15 c.c.). The anhydride, prepared by heating with acetic anhydride, diluting with water, and extracting with ether, separated from the ether in beautiful plates, m. p. 252—254° (Pope and Kipping's *trans*-camphotricarboxylic acid melts at 195—196° [decomp.], has $[\alpha]_D + 37·2°$ in alcohol, and gives an anhydride, m. p. 253—254°).

The benzene extract gave a crystalline by-product, m. p. about 202° (decomp.), $[\alpha]_{5461} + 19·4°$ in acetone (2·166 g. per 100 c.c.).

This was expected to be a π-chlorodinitro-α-bromocamphor; but, unlike the compound which Wedekind obtained under analogous conditions, it was soluble in alkalis, as if it contained a primary or secondary, instead of only tertiary, nitro-groups. Moreover, it appeared to contain an additional molecule of water, although there was not enough material available to confirm the analysis. Since the constitution of the compound is still unknown, it is hoped to investigate it more fully later.

Attempt to Make Toluene-o-chlorosulphoxide.—o-Toluenesulphonyl chloride (14 c.c.) was heated with dry piperidine (11 g.) for 1½ hours, the liquid becoming of an intense dark red colour as in the case of α-bromocamphor-π-sulphonyl chloride. After washing with acidified water, extracting with ether, and drying over calcium chloride, the oil was distilled in a vacuum, 85% of the o-toluenesulphonyl chloride being recovered unchanged. The charred residue was not investigated.

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CAMBRIDGE.   [*Received, November 18th, 1924.*]

XLVI.—*Conversion of Amino-acids into Tertiary Amino-alcohols.*

By ALEX. MCKENZIE and GEORGE OGILVIE WILLS.

THE first application of Grignard reagents towards esters of amino-acids was made by Baeyer and Villiger (*Ber.*, 1904, **37**, 3191), who converted methyl anthranilate into o-aminotriphenylcarbinol by means of magnesium phenyl bromide. Paal and Weidenkaff (*Ber.*, 1905, **38**, 1686) obtained β-amino-αα-diphenylethyl alcohol from ethyl glycine (compare also Paal and Weidenkaff, *Ber.*, 1906, **39**, 810, 4344; Krassusky, *Compt. rend.*, 1908, **146**, 236).

The Grignard reaction has been also applied in this laboratory for preparing amino-alcohols in connexion with the study of semipinacolinic deamination. Since other workers (Thomas and Bettzieche, *Z. physiol. Chem.*, 1924, **140**, 244, 261, 279; Bettzieche, *ibid.*, 273) have entered the same field quite recently, we think it desirable to describe our further results.

The elimination of the amino-group in tertiary amino-alcohols has been dealt with (McKenzie and Richardson, *J.*, 1923, **123**, 79; McKenzie and Roger, *J.*, 1924, **125**, 844; McKenzie and Dennler, *J.*, 1924, **125**, 2105). The first instance described in the literature as a semipinacolinic deamination arose from the accidental discovery that the transformation $OH \cdot CPh_2 \cdot CHPh \cdot NH_2 \rightarrow OH \cdot CPh_2 \cdot CHPh \cdot OH$

could *not* be effected by the agency of nitrous acid; the product of the action was phenyldeoxybenzoin and *not* triphenylethylene glycol. β-Amino-ααβ-triphenylethyl alcohol was prepared by McKenzie and Barrow (J., 1913, **103**, 1331) by the action of magnesium phenyl bromide on *r*-desylamine hydrochloride and later on *r*-phenylaminoacetic acid by McKenzie and Richardson. Thomas and Bettzieche have repeated its preparation from phenylaminoacetic acid, and confirmed the conversion into phenyldeoxybenzoin. The conversion of *r*-phenylalanine into *r*-β-amino-β-benzyl-αα-diphenylethyl alcohol

$$\underset{H}{\overset{CH_2Ph}{>}}C{-}CO_2Ph \rightarrow \underset{H}{\overset{CH_2Ph}{>}}\underset{NH_2}{C}{-}\underset{OH}{C}\underset{Ph}{\overset{Ph}{<}}$$
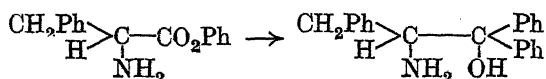
was also carried out in this laboratory and it was shown that the amino-alcohol undergoes semipinacolinic deamination :

$$CH_2Ph{\cdot}\underset{NH_2}{\overset{H}{C}}\quad\underset{OH}{\overset{Ph}{C}}{\cdot}Ph \xrightarrow{\text{(by HNO}_2\text{)}} CH_2Ph{\cdot}\underset{N{:}N{-}OH}{\overset{H}{C}}{-}\underset{OH}{\overset{Ph}{C}}{\cdot}Ph \rightarrow$$

$$CH_2Ph{\cdot}\underset{{\cdot}O}{CH}{-}\overset{Ph}{C}{\cdot}Ph \rightarrow \underset{Ph}{\overset{CH_2Ph}{>}}CH{\cdot}CO{\cdot}Ph.$$
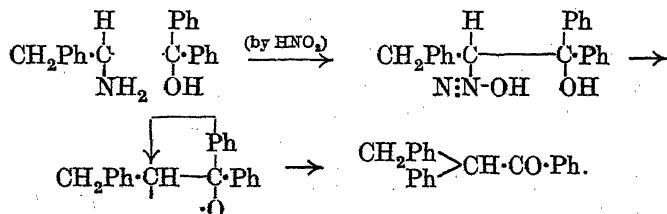
The phenyl group migrates, and the product is benzyldeoxybenzoin. Those results are also confirmed by Thomas and Bettzieche.

According to Paal and Weidenkaff (*loc. cit.*), the action of nitrous acid on β-amino-αα-diphenylethyl alcohol leads to the formation of *as*-diphenylethylene oxide :

$$\underset{Ph}{\overset{Ph}{>}}\underset{OH}{C}{-}\underset{NH_2}{C}\underset{H}{\overset{H}{<}} \rightarrow \underset{Ph}{\overset{Ph}{>}}C{-}C\underset{H}{\overset{H}{<}}{\cdot}$$
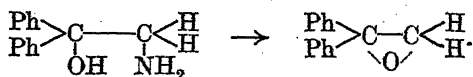
In the light of our work on semipinacolinic deamination, it seemed possible that this conclusion was erroneous, and that the product was actually deoxybenzoin. By arrangement with us, Professor Tiffeneau and M. Orékhov had kindly undertaken the investigation of this point, which meanwhile has been solved by Bettzieche. The product is deoxybenzoin, and we would interpret its formation on the following lines, the phenyl group migrating thus :

$$\underset{Ph}{\overset{Ph}{>}}\underset{OH}{C}{-}\underset{H_2N}{C}\underset{H}{\overset{H}{<}} \rightarrow \underset{Ph}{\overset{Ph}{>}}\underset{OH}{C}{-}\underset{OH{\cdot}N{:}N}{C}\underset{H}{\overset{H}{<}}$$

$$\rightarrow \underset{Ph}{\overset{Ph}{>}}\underset{O{\cdot}}{C}{-}\underset{}{C}\underset{H}{\overset{H}{<}} \rightarrow Ph{\cdot}CO{\cdot}CH_2Ph.$$
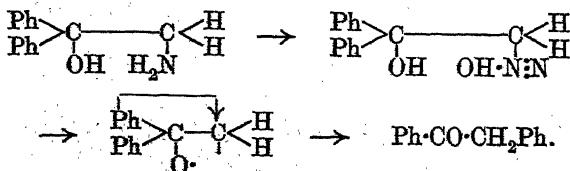
In a former paper, we mentioned that we were continuing our study of the action of nitrous acid on compounds containing the group $>\underset{\underset{OH}{|}}{C}\!\!-\!\!\underset{\underset{NH_2}{|}}{C}<$ with the object of extending our experience ultimately to optically active amino-alcohols. Accordingly in the present paper we describe the action of magnesium phenyl bromide on *r*-alanine, thus :

$$CO_2H\cdot\underset{\underset{H_2N}{|}}{C}<\!\!\overset{Me}{\underset{H}{}} \quad \rightarrow \quad \overset{Ph}{\underset{Ph}{}}\!\!>\underset{\underset{OH}{|}}{C}\!\!-\!\!-\!\!\underset{\underset{H_2N}{|}}{C}<\!\!\overset{Me}{\underset{H}{}}$$
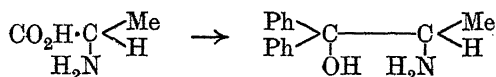
The amino-alcohol on deamination gave methyldeoxybenzoin :

$$\overset{Ph}{\underset{Ph}{}}\!\!>\underset{\underset{OH}{|}}{C}\!\!-\!\!-\!\!\underset{\underset{H_2N}{|}}{C}<\!\!\overset{Me}{\underset{H}{}} \quad \rightarrow \quad \overset{Ph}{\underset{Ph}{}}\!\!>\underset{\underset{OH}{|}}{C}\!\!-\!\!-\!\!\underset{\underset{OH\cdot N\colon N}{|}}{C}<\!\!\overset{Me}{\underset{H}{}}$$

$$\rightarrow \quad \overset{Ph}{\underset{Ph}{}}\!\!>\underset{\underset{O\cdot}{|}}{C}\!\!-\!\!\underset{|}{C}<\!\!\overset{Me}{\underset{H}{}} \quad \rightarrow \quad Ph\cdot CO\cdot CH<\!\!\overset{Me}{\underset{Ph}{}},$$
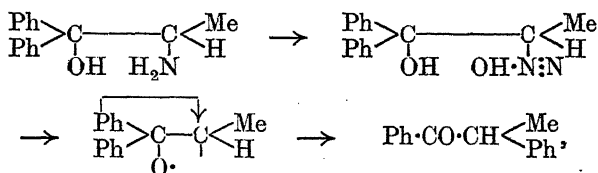
and thus provided another instance of the striking regularity with which the phenyl group migrates in all the cases of semipinacolinic deamination which have been studied.

The change may be contrasted with the vinyl dehydration of *r*-methylhydrobenzoin studied by Tiffeneau and Orékhov (*Bull. Soc. chim.*, 1921, [iv], **29**, 422), and by McKenzie and Roger incidentally to their work on the dehydration of optically active methylhydrobenzoin by concentrated sulphuric acid :

$$\overset{Ph}{\underset{H}{}}\!\!>\underset{\underset{OH}{|}}{C}\!\!-\!\!-\!\!\underset{\underset{HO}{|}}{C}<\!\!\overset{Me}{\underset{Ph}{}} \quad \rightarrow \quad Ph\cdot CO\cdot CH<\!\!\overset{Me}{\underset{Ph}{}}.$$
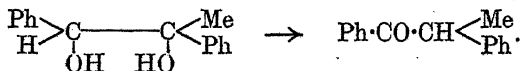
The above result has already been arrived at by Bettzieche, who carried out the action with a trace of the amino-alcohol. In the light of the work of McKenzie and Roger as applied to the optically active methyl- and ethyl-hydrobenzoins, the extension of this action to the optically active amino-alcohol derived from *d*-alanine presents obvious points of interest, and we are at present engaged in the investigation of this topic.

As already stated, the action of nitrous acid on β-amino-ααβ-triphenylethyl alcohol had been examined with the object of obtaining triphenylethylene glycol. The optically active forms of the latter compound had already been described (McKenzie and Wren, J., 1910, **97**, 473; McKenzie, Drew, and Martin, J., 1915, **107**, 26), and the change in question, if carried out with the optically active amino-alcohols, would have provided data in connexion with the Walden inversion. This scheme, however,

cannot be effected in practice for the reasons already given.   Nevertheless, we have thought it desirable that the optically active amino-alcohols should at least be prepared.   The description of their preparation is now given in the experimental part.   The compounds in question are highly active, giving $[\alpha]_D \pm 243°$ in chloroform ;   they rotate the plane of polarisation in the opposite sense to the phenylaminoacetic acids from which they are prepared. There is no configurative change here, however, since there is no substitution of a group directly attached to the asymmetric carbon atom, so that the compound which is derived from d-phenylamino-acetic acid is designated as d-β-amino-$\alpha\alpha\beta$-triphenylethyl alcohol, although it is lævorotatory, d-phenylaminoacetic acid being taken as the reference type.   It is rather curious to note that a similar change of sign of rotation also occurs when methyl l-mandelate is converted by magnesium phenyl bromide into triphenylethylene glycol (McKenzie and Wren, *loc. cit.*).

The action of nitrous acid on the d-amino-alcohol gives an optically inactive product owing to semipinacolinic deamination, the product being phenyldeoxybenzoin.

The isomeric camphorsulphonates of the d- and l-amino-alcohols were prepared, but the resolution of the r-alcohol by d-camphor-β-sulphonic acid gave a very slow and imperfect separation, and the method was obviously unsatisfactory.   We are at present engaged in resolving by means of camphorsulphonic acids the r-amino-alcohols related to desylamine.

The changes

$$\underset{Me}{\overset{Ph}{>}}C\underset{CO_2H}{\overset{NH_2}{<}} \longrightarrow \underset{Me}{\overset{Ph}{>}}\underset{\underset{NH_2}{|}}{C}\text{———}\underset{\underset{HO}{|}}{C}\underset{Ph}{\overset{Ph}{<}}$$

and $d\text{-} CH_2Ph\cdot CH(NH_2)\cdot CO_2H \longrightarrow d\text{-} \underset{H}{\overset{CH_2Ph}{>}}\underset{\underset{NH_2}{|}}{C}\text{———}\underset{\underset{HO}{|}}{C}\underset{Ph}{\overset{Ph}{<}}$
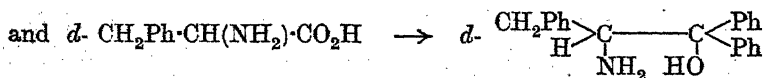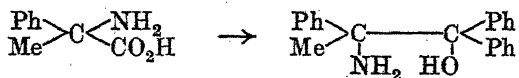
are also described, but the study of the action of nitrous acid on the amino-alcohols has not yet been completed.

Arising from the present research, the following points have been investigated.   The ethyl ester hydrochloride of l-phenyl-aminoacetic acid gives on hydrolysis with a slight excess of alcoholic potash a phenylaminoacetic acid with $[\alpha]_D - 12\cdot4°$ in hydrochloric acid solution, whereas the pure l-acid has $[\alpha]_D - 157\cdot8°$ in the same solvent.   This result was anticipated, since in phenylaminoacetic acid we have both a phenyl group and a migrational hydrogen atom in direct attachment to the asymmetric carbon atom.

McKenzie and Walker (J., 1915, **107**, 1685) have shown that catalytic racemisation occurs when l-phenylbromoacetic acid is

acted on by ammonia. When the action was conducted in benzene solution, that portion of the bromo-acid which had survived the attack of the ammonia had become largely racemised. It was thought possible that something of the same kind might occur when *l*-phenylaminoacetic acid is acted on by nitrous acid; such, however, is not the case.

There was one other rather important point in connexion with the study of the Walden inversion in the mandelic acid series which clearly required elucidation. E. Fischer and Weichhold (*Ber.*, 1908, **41**, 1286) acted on ethyl *d*-phenylaminoacetate with nitrous acid and obtained *a change of sign* of rotation, the resulting ethyl mandelate being highly racemised, and lævorotatory. On the other hand, Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2259), by acting on a solution of the hydrochloride of ethyl *l*-phenylaminoacetate in dilute sulphuric acid with nitrous acid, obtained an ethyl mandelate of *the same sign* of rotation as that of the original ethyl *l*-phenylaminoacetate. We have repeated the work both of Fischer and Weichhold and of Marvel and Noyes, and have found that a change of sign of rotation occurs when ethyl *l*-phenylaminoacetate is acted on by nitrous acid if the solution, before the ester is extracted, is kept sufficiently long after the addition of the nitrite. Fischer and Weichhold's conclusion,

$$d\text{-CHPh(NH}_2)\cdot\text{CO}_2\text{Et} \longrightarrow l\text{-CHPh(OH)}\cdot\text{CO}_2\text{Et},$$
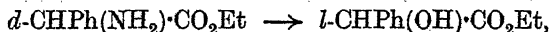
is therefore correct. Since McKenzie and Clough (J., 1909, **95**, 777) have shown that the change

$$d\text{-CHPh(NH}_2)\cdot\text{CO}_2\text{H} \longrightarrow l\text{-CHPh(OH)}\cdot\text{CO}_2\text{H}$$
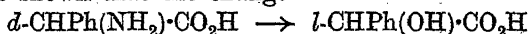
occurs, the behaviour both of the ester and of the free acid towards nitrous acid is similar. The product obtained by the method of the American workers was contaminated with a nitrogenous compound (probably a diazo-compound). It seems that they had proceeded to isolate their ethyl mandelate too quickly after the addition of the sodium nitrite.

The work on the action of nitrous acid on compounds containing the grouping $\underset{\text{OH}\ \ \text{NH}_2}{>\!\text{C}\!-\!\text{C}\!<}$ is being continued.

EXPERIMENTAL.

Semipinacolinic Deamination of β-*Amino-αα-diphenyl-*n-*propyl Alcohol.*—Ethyl *r*-alanine hydrochloride (compare Curtius and Koch, *J. pr. Chem.*, 1888, [ii], **38**, 472; Barker and Skinner, *J. Amer. Chem. Soc.*, 1924, **46**, 403) was conveniently prepared as follows : A current of dry hydrogen chloride was passed into a suspension of *r*-alanine (10 g.) in ethyl alcohol (200 c.c.) for 1 hour, and the mixture, after boiling for 1 hour longer, was evaporated

to dryness at the ordinary temperature under 15 mm. pressure. The resulting syrup solidified when kept over soda–lime in a vacuum. It crystallised from ethyl acetate in needles (15·5 g.; 90% of the theoretical). Ethyl r-alanine hydrochloride (20 g.) was added gradually to the Grignard reagent prepared from bromobenzene (245 g.), and the mixture heated for 8 hours. The product was decomposed by ice, ammonium chloride and ammonia. The residual solid was extracted with ether and added to the main ethereal solution. After removal of ether and diphenyl as usual, the product (20 g.) was dissolved in hydrochloric acid and precipitated by ammonia. This treatment was repeated and then the product was crystallised three times from aqueous alcohol.

β-*Amino*-αα-*diphenyl*-n-*propyl alcohol* separates from aqueous alcohol in rhombohedral plates, m. p. 101·5—102·5°, is readily soluble in ethyl alcohol, methyl alcohol, benzene, toluene, carbon tetrachloride, carbon disulphide, acetone, or ether, and very sparingly soluble in water (Found : C = 79·4; H = 7·7; N = 6·2. $C_{15}H_{17}ON$ requires C = 79·3; H = 7·5; N = 6·2%). A trace added to concentrated sulphuric acid assumes a golden-yellow tint, and the solution becomes at first pink and quickly colourless.

A solution of 4·5 g. of sodium nitrite in 20 c.c. of water was gradually added (¾ hour) to a solution of 5 g. of the amino-alcohol in 150 c.c. of 25% acetic acid, cooled at 0°. A flocculent precipitate was gradually deposited, which was filtered off after 24 hours, and crystallised from aqueous alcohol. The silky needles (m. p. 50—51°) which separated amounted to 4 g., and were identified as methyldeoxybenzoin (Found : C = 85·8; H = 7·0. Calc., C = 85·7; H = 6·7%). There was no depression of the melting point when this substance was mixed with a specimen of the methyldeoxybenzoin prepared by McKenzie and Roger (J., 1924, **125**, 844) by the dehydration of methylhydrobenzoin with concentrated sulphuric acid. The coloration observed with concentrated sulphuric acid was identical with that described by McKenzie and Roger for their product. The identity of the substance was also proved by its behaviour towards magnesium phenyl bromide, when ααβ-triphenylpropyl alcohol, m. p. 86·5—87·5°, was isolated. The latter compound had already been prepared by Mlle Lévy (*Bull. Soc. chim.*, 1921, [iv], **29**, 878) and by McKenzie and Roger.

Hydrochlorides of Ethyl d- *and* l-*Phenylaminoacetates.*—The optically active phenylaminoacetic acids were prepared by E. Fischer and Weichhold (*Ber.*, 1908, **41**, 1286), who resolved the formyl r-acid by cinchonine and quinine and then hydrolysed the d- and l-formyl acids with hydrobromic acid. The resolution of

r-phenylaminoacetic acid into its optically active components by means of Reychler's d-camphor-β-sulphonic acid in aqueous solution has been described by Betti and Mayer (*Ber.*, 1908, **41**, 2071) and by Marvel and Noyes (*J. Amer. Chem. Soc.*, 1920, **42**, 2259), the acids being employed in equimolecular quantities. In the modification described by Ingersoll and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 2930), an excess of the camphorsulphonic acid was used. Since the latter acid contains water of crystallisation (Pope and Gibson, J., 1910, **97**, 2211), and, since this may possibly be present in varying quantity, we employed this method. The optically pure l-acid was obtained by adding the requisite amount of ammonia to the solution of the salt obtained after several crystallisations. The d-acid may be prepared from the acid mixture obtained from the first mother-liquor of the preceding resolution either by means of d-α-bromocamphor-β-sulphonic acid or by formylating and then converting into the quinine salt. For the purification of the d-acid, however, it is more convenient to combine the crude acid with l-camphor-β-sulphonic acid, and then to crystallise until the camphorsulphonate is homogeneous. We were enabled to conduct the resolution in the latter manner owing to the generous gift of a supply of l-camphor from Sir William Pope. The l-camphorsulphonic acid, obtained from l-camphor by sulphonation in presence of acetic anhydride, was crystallised from ethyl acetate and gave in aqueous solution : $l = 2$, $c = 3\cdot8705$, $\alpha_D - 1\cdot61°$, $[\alpha]_D - 20\cdot8°$.

l-Camphorsulphonic acid combines with l-phenylaminoacetic acid to form a salt which is readily soluble in water, from which it separates in prisms. Its rotation was determined in aqueous solution : $l = 2$, $c = 4\cdot630$, $\alpha_D - 6\cdot64°$, $[\alpha]_D - 71\cdot7°$.

The diastereoisomeric salt, prepared from d-camphorsulphonic acid and l-phenylaminoacetic acid, has $[\alpha]_D - 44\cdot07°$ ($c = 2\cdot0885$, $l = 2$) in aqueous solution (Betti and Mayer, *loc. cit.*). This value enabled us to estimate the progress of the resolution of r-phenylaminoacetic acid by d- and l-camphorsulphonic acids. The polarimetric values for the l- and d-phenylaminoacetic acids obtained agreed with those of Fischer and Weichhold.

Ethyl l-*Phenylaminoacetate Hydrochloride.*—Fischer and Weichhold describe the conversion of l-phenylaminoacetic acid into the hydrochloride of its ethyl ester, which they describe as dextrorotatory, $[\alpha]_D^{20} + 88\cdot95°$ in aqueous solution ($p = 5\cdot021$, $d_4^{18} = 1\cdot0097$). Our results were different. For example, a current of dry hydrogen chloride was passed into a mixture of 3·3 g. of l-phenylaminoacetic acid and 40 c.c. of ethyl alcohol for 1½ hours. The solution was then boiled for a few minutes, and filtered from a

small amount of solid. The alcohol was removed from the filtrate by gentle warming under diminished pressure, the resulting acid dissolved in 20 c.c. of water, and an equal volume of benzene added. The addition of the requisite amount of ammonia caused the separation of the ester, which was extracted with benzene. A current of dry hydrogen chloride was passed into the benzene solution for 15 minutes, when the crystalline ester hydrochloride (4·2 g.) separated. It had the following rotation in aqueous solution : $l = 1$, $c = 5·070$, $\alpha_D - 4·53°$, $[\alpha]_D - 89·3°$.

Marvel and Noyes also obtained a lævorotatory ester hydrochloride with $[\alpha]_D - 84·6°$ (concentration not quoted) from the l-amino-acid. The dextrorotation recorded by Fischer and Weichhold is possibly due to a typographical error.

Ethyl d-*phenylaminoacetate hydrochloride* was prepared in a similar manner from d-phenylaminoacetic acid, 6·1 g. being obtained from 5·8 g. of d-acid. It was dextrorotatory in aqueous solution: $l = 1$, $c = 5·070$, $\alpha_D + 4·60°$, $[\alpha]_D + 90·7°$.

Action of Magnesium Phenyl Bromide on the Hydrochlorides of Ethyl d- *and* l-*Phenylaminoacetate.*—The d-ester hydrochloride (6 g.; 1 mol.) was gradually added within 15 minutes to the Grignard reagent prepared from 52 g. of bromobenzene (12 mols.), 16·5 g. of magnesium and 350 c.c. of ether, and the mixture heated for $4\frac{1}{2}$ hours. After decomposition of the product with ice and ammonium chloride, and remaining over-night, the ethereal layer was separated and the aqueous layer extracted with ether. The ether and the diphenyl were removed, the latter by steam distillation. The residual yellow solid (8 g.) was crystallised from ethyl alcohol until the product, after drying over concentrated sulphuric acid in a vacuum until constant, gave a value which remained unchanged on polarimetric examination after repeated crystallisation.

d-β-*Amino-ααβ-triphenylethyl alcohol* is somewhat sparingly soluble in ethyl alcohol and separates in colourless needles, m. p. 129·5—130°, whereas the r-isomeride (McKenzie and Barrow, J., 1913, **103**, 1331) melts at 154·5—155°. A trace of it added to concentrated sulphuric acid gives a pink coloration which quickly becomes orange-brown. It is readily soluble in chloroform, ether, benzene or acetone (Found : C = 83·1; H = 6·8. $C_{20}H_{19}ON$ requires C = 83·0; H = 6·6%).

The substance has the opposite sign of rotation to the original ester hydrochloride, being strongly lævorotatory in chloroform : $l = 2$, $c = 1·276$, $\alpha_D^{15°} - 6·19°$, $[\alpha]_D^{15°} - 243°$. In benzene : $l = 2$, $c = 2·027$, $\alpha_D^{17°} - 9·45°$, $[\alpha]_D^{17·5°} - 233°$.

The l-ester hydrochloride (5 g.) was acted on by magnesium

phenyl bromide under conditions similar to those just described. Yield of crude amino-alcohol = 6 g. It was purified by crystallis-ation from ethyl alcohol.

l-β-*Amino-ααβ-triphenylethyl alcohol* has m. p. 129·5—130° (Found : N = 4·9. $C_{20}H_{19}ON$ requires N = 4·8%). The compound is strongly dextrorotatory in chloroform : $l = 2$, $c = 1·304$, $\alpha_D^{15·5°} + 6·34°$, $[\alpha]_D^{15·5°} + 243°$. $l = 2$, $c = 1·304$, $\alpha_{5461}^{15°} + 7·63°$, $[\alpha]_{5461}^{15°} + 293°$. In benzene : $l = 2$, $c = 2·017$, $\alpha_D^{16°} + 9·44°$, $[\alpha]_D^{16°} + 234°$.

Action of Nitrous Acid on d-β-*Amino-ααβ-triphenylethyl Alcohol.*— A solution of the d-amino-alcohol (0·68 g.) in 50 c.c. of dilute acetic acid was cooled in a freezing mixture of ice and salt, and a solution of 0·5 g. of sodium nitrite in 5 c.c. of water added during 20 minutes. The solid (0·6 g.) which separated was crystallised from ethyl alcohol, and 0·42 g. of phenyldeoxybenzoin, needles, m. p. 134—135°, was obtained. It gave the characteristic emerald-green coloration with concentrated sulphuric acid. Its solution in chloro-form was optically inactive.

Isomeric Camphorsulphonates of the d- *and* l-*Amino-Alcohols.*— l-β-*Amino-ααβ-triphenylethanol* d-*camphorsulphonate*, prepared by combining the l-amino-alcohol (1 mol.) with d-camphor-β-sulphonic acid (1 mol.) in ethyl-alcoholic solution, separates in needles, m. p. 200—201° (decomp.) (Found : S = 6·3. $C_{10}H_{16}O_4S$ requires S = 6·1%). In ethyl alcohol : $l = 2$, $c = 0·8568$, $\alpha_D^{17°} + 2·08°$, $[\alpha]_D^{17°} + 121°$; $l = 2$, $c = 0·8568$, $\alpha_{5461}^{15·5°} + 2·41°$, $[\alpha]_{5462}^{15·5°} + 143°$.

The enantiomorphously related d-β-*amino-ααβ-triphenylethanol* l-*camphorsulphonate* separates from ethyl alcohol in needles, m. p. 200—201° (decomp.) (Found : N = 2·9. $C_{20}H_{18}ON$ requires N = 2·7%). In ethyl alcohol : $l = 2$, $c = 0·80$, $\alpha_D^{16°} - 1·91°$, $[\alpha]_D^{16°} - 119°$; $l = 2$, $c = 0·80$, $\alpha_{5461}^{15°} - 2·31°$, $[\alpha]_{5461}^{15°} - 144°$.

l-β-*Amino-ααβ-triphenylethanol* l-*camphorsulphonate* separates from ethyl alcohol in needles, m. p. 213·5—214·5° (decomp.). In ethyl alcohol : $l = 2$, $c = 0·4448$, $\alpha_D^{16·5°} + 0·68°$, $[\alpha]_D^{16·5°} + 76°$; $l = 2$, $c = 0·4448$, $\alpha_{5461}^{16°} + 0·76°$, $[\alpha]_{5461}^{16°} + 85°$.

The enantiomorphously related d-β-*amino-ααβ-triphenylethanol* d-*camphorsulphonate* separates from ethyl alcohol in needles, m. p. 213·5—214·5° (decomp.) (Found : S = 6·2. $C_{10}H_{16}O_4S$ requires S = 6·1%). In ethyl alcohol : $l = 2$, $c = 0·40$, $\alpha_D^{16°} - 0·61°$, $[\alpha]_D^{16°} - 76°$; $l = 2$, $c = 0·40$, $\alpha_{5461}^{15°} - 0·72°$, $[\alpha]_{5461}^{15°} - 90°$.

It is insoluble in most organic solvents, moderately soluble in hot ethyl alcohol or water, and sparingly soluble in these solvents at the ordinary temperature. The concentrations employed in the determination of specific rotatory power were necessarily low, so that the values for the specific rotatory power have little significance.

Attempts were made to resolve the r-amino-alcohol by d-camphor-

β-sulphonic acid both in aqueous and ethyl-alcoholic solution. The progress of the resolution was, however, too slow to enable the method to be used as a preparative one for the d- and l-amino-alcohols.

Action of Magnesium Phenyl Bromide on α-Aminohydratropic Acid.—The amino-acid (6 g.; 1 mol.), prepared according to McKenzie and Clough (J., 1912, **101**, 390), was added in instalments (½ hour) to the Grignard reagent (12 mols.) prepared from bromobenzene (71 g.), and the mixture was heated for 10½ hours. After decomposition with ice and ammonium chloride, the remaining solid was extracted with ether and the solution added to the main ethereal solution. The ether and diphenyl were removed; the resulting oil solidified. Yield : 5 g. It was triturated with light petroleum, and the solid then crystallised from rectified spirit until pure. Yield : 2 g.

β-*Amino-ααβ-triphenyl-β-methylethyl alcohol* separates from rectified spirit in rectangular plates, is soluble in benzene and chloroform, and melts at 113—114° (Found : C = 83·0; H = 7·2; N = 4·8. $C_{21}H_{21}ON$ requires C = 83·1; H = 7·0; N = 4·6%). A trace of this compound added to concentrated sulphuric acid produces an orange coloration, which changes quickly to a permanent crimson colour.

Action of Magnesium Phenyl Bromide on r-Phenylalanine.—No visible action took place when r-phenylalanine (3 g.; 1 mol.) was gradually added to the Grignard reagent (12 mols.) prepared from 34 g. of bromobenzene. The mixture was heated for 20 hours, and then the additive compound was decomposed with ice and ammonium chloride. The ethereal layer was withdrawn, and then the ether and diphenyl were removed from it in the usual manner. The residual solid amounted to 4 g., which were crystallised from ethyl alcohol. The yield of pure amino-alcohol was 2·4 g., corresponding in crystalline form and melting point with r-β-amino-αα-diphenyl-β-benzylethyl alcohol, which was prepared by McKenzie and Richardson (J., 1923, **123**, 79) from the ethyl ester hydrochloride of phenylalanine by the action of magnesium phenyl bromide.

Action of Magnesium Phenyl Bromide on d-*Phenylalanine.*—r-Phenylalanine was resolved by the alkaloidal method of E. Fischer and Schoeller (*Annalen*, 1907, **357**, 2), and d-phenylalanine was isolated with a specific rotation in aqueous solution of + 35·0° (l = 2, c = 2·043, $α_D$ + 1·43°), this value being identical with that quoted by Fischer and Schoeller. Three g. of this amino-acid were treated in the manner recorded in the above experiment, with the exception that the mixture was heated for 24 instead of

20 hours. 4·2 G. of crude amino-alcohol were obtained, and were crystallised from ethyl alcohol several times until a steady value for the specific rotation was obtained in chloroform : $l = 2$, $c =$ 2·0472, $\alpha_D^{16\cdot5^\circ} + 3\cdot48^\circ$, $[\alpha]_D^{16\cdot5^\circ} + 85\cdot0^\circ$; $l = 2$, $c = 2\cdot0472$, $\alpha_{5461}^{18\cdot5^\circ} +$ 4·06°, $[\alpha]_{5461}^{18\cdot5^\circ} + 99\cdot2^\circ$. In benzene : $l = 2, c = 2\cdot0512$, $\alpha_D^{19^\circ} + 4\cdot32^\circ$, $[\alpha]_D^{19^\circ} + 105\cdot3^\circ$; $l = 2$, $c = 2\cdot0512$, $\alpha_{5461}^{15^\circ} + 5\cdot03^\circ$, $[\alpha]_{5461}^{15^\circ} + 122\cdot6^\circ$.

This compound has the same sign of rotation as the original amino-acid, and, since no configurative change can take place in the transformation of the amino-acid into the amino-alcohol, it is accordingly designated as d-β-*amino-αα-diphenyl-β-benzylethyl alcohol*. It crystallises from ethyl alcohol in flat, glassy needles, m. p. 143— 144°, is soluble in acetone, benzene, chloroform, ether, or toluene, but is insoluble in water (Found : $N = 4\cdot6$. $C_{21}H_{21}ON$ requires $N = 4\cdot6\%$). A trace of the compound added to concentrated sulphuric acid produces an orange-brown coloration, which quickly changes to pale pink and then gradually fades. This coloration is also observed with the corresponding r-amino-alcohol.

Hydrolysis of Ethyl l-*Phenylaminoacetate Hydrochloride.*—The l-ester hydrochloride (1 g.) in 30 c.c. of ethyl-alcoholic potassium hydroxide (0·4487N) remained for 24 hours at the ordinary temperature, and was then heated on the water-bath for 30 minutes. The alcohol was removed under diminished pressure, the residue dissolved in water, and the solution extracted with benzene to remove any trace of unchanged ester. The aqueous solution was then neutralised with hydrochloric acid, and the amino-acid (0·5 g.) was separated. Its specific rotation was determined as follows : 0·3719 g. was dissolved in 3·35 c.c. of N-hydrochloric acid and 1·5 c.c. of water, $l = 0\cdot5, p = 7\cdot193, d_4^{20} = 1\cdot0286$, $\alpha_D - 0\cdot46^\circ$, $[\alpha]_D - 12\cdot4^\circ$. The ester hydrochloride was completely hydrolysed.

Partial Deamination of l-*Phenylaminoacetic Acid.*—A solution of sodium nitrite (0·41 g.) in water (2 c.c.) was added drop by drop (30 minutes) to a solution of the l-amino-acid (2 g.) in N-sulphuric acid (30 c.c.) at 0°. After 5 hours at 0° and 18 hours at the ordinary temperature, the amino-acid (1·35 g.) was precipitated by the addition of ammonia in slight excess. 0·7438 G. was dissolved in 6·7 c.c. of N-hydrochloric acid and 3 c.c. of water, $l = 1, p =$ 7·193, $d_4^{20} = 1\cdot0286$, $\alpha_D - 11\cdot36^\circ$, $[[\alpha]_D - 153\cdot5^\circ$, whereas the original l-acid had $[\alpha]_D - 156^\circ$ under similar conditions.

The ammoniacal solution, from which the amino-acid had been separated, was acidified with dilute hydrochloric acid, and extracted with ether. The resulting mandelic acid (0·23 g.) was slightly dextrorotatory in aqueous solution : $l = 2$, $c = 1\cdot055$, $\alpha_D + 0\cdot13^\circ$.

Deamination of Ethyl l-*Phenylaminoacetate.*—*Method of E. Fischer and Weichhold.* These authors acted on the d-ester with nitrous

acid and obtained a lævorotatory ethyl mandelate with about $[\alpha]_D - 10°$ in acetone solution. On following their directions, using ethyl l-phenylaminoacetate (0·90 g.) in place of the d-ester, the resulting mandelic ester (0·325 g.) was dextrorotatory. A 10% solution gave $\alpha_D + 0·45°$ in a 0·5 dcm.-tube, so that the value for the specific rotation is approximately $+ 9°$. The result of Fischer and Weichhold was thus confirmed. It should be stated that after the addition of the nitrite, the solution remained over-night at the ordinary temperature. The large amount of racemisation which accompanied this change is apparent when it is recalled that ethyl l-mandelate has, according to Walden (*Z. physikal. Chem.*, 1895, **17**, 705), $[\alpha]_D - 90·6°$ in acetone solution.

The dextrorotatory ester obtained above gave a negative result when tested for nitrogen. It was hydrolysed by 4·5 c.c. of aqueous potassium hydroxide (0·5755N) at the ordinary temperature for 18 hours. The solution was extracted with ether to remove any unsaponified ester, and the mandelic acid isolated from the aqueous solution as usual. The resulting acid (0·14 g.) was dextrorotatory in aqueous solution: $l = 2$, $c = 0·622$, $\alpha_D + 0·27°$.

Method of Marvel and Noyes. A solution of sodium nitrite (1·6 g.) in water (2·5 c.c.) was added drop by drop with constant stirring for 30 minutes to a solution of ethyl l-phenylaminoacetate hydrochloride (5·4 g.) in N-sulphuric acid (33 c.c.), the temperature being kept at 0° throughout. A yellow oil separated. After 1 hour at 0° and 2 hours at the ordinary temperature, the solution was extracted with ether, the ethereal solution dried with anhydrous sodium sulphate, and the ether expelled. The resulting oil was distilled, and the portion (1·5 g.) b. p. 127—132°/18 mm. collected. In acetone: $l = 2$, $c = 10$, $\alpha_D - 0·35°$.

The product obtained by Marvel and Noyes was also lævo-rotatory.

When this oil was tested for nitrogen, it gave a positive result. On hydrolysis under conditions similar to those described in the previous experiment, it gave a mandelic acid (0·8 g.) which was slightly dextrorotatory in aqueous solution: $l = 2$, $c = 3·109$, $\alpha_D + 0·10°$.

This shows that the lævorotation observed by Marvel and Noyes was not due to ethyl l-mandelate, but rather to the presence of an intermediate lævorotatory diazo-compound, which gradually passes into ethyl d-mandelate with lapse of time. That this view is probable appears from the result of the second experiment quoted below.

The unattacked ethyl phenylaminoacetate hydrochloride was recovered from the aqueous solution remaining after the extraction

of the deamination product with ether. The solution was made alkaline with ammonia, extracted with benzene, the benzene solution dried, and dry hydrogen chloride passed in to precipitate the ester hydrochloride. The latter was filtered off. Yield : 2 g. In aqueous solution : $l = 1$, $c = 5 \cdot 07$, $\alpha_D - 4 \cdot 59°$, $[\alpha]_D - 90 \cdot 5°$. The regenerated hydrochloride had thus practically the same rotation as the original.

In a second experiment where 7 g. of the l-ester hydrochloride were employed, the conditions of deamination were exactly similar to those just described except that the solution after being kept at 0° was allowed to remain for $3\frac{1}{2}$ instead of 2 hours. The resulting oil (2 g.), which gave a positive test for nitrogen, was in this case dextrorotatory in acetone solution : $l = 1$, $c = 10$, $\alpha_D + 0 \cdot 30°$.

On hydrolysis with aqueous alkali under similar conditions to those adopted in the other experiments, the resulting mandelic acid was dextrorotatory in aqueous solution : $l = 2$, $c = 3 \cdot 32$, $\alpha_D + 0 \cdot 19°$.

The amino-ester hydrochloride was recovered as before. In aqueous solution : $l = 1$, $c = 5 \cdot 07$, $\alpha_D - 4 \cdot 57°$, $[\alpha]_D - 90 \cdot 1°$.

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XLVII.—The Action of Caustic Alkali on α-Bromo-α-ethylbutyrylcarbamide.

By GEORGE NEWBERY.

THE action of water, caustic alkali and of pyridine on α-bromo-α-ethylbutyrylcarbamide (adalin), $CBrEt_2 \cdot CO \cdot NH \cdot CO \cdot NH_2$, was investigated by Rosenmund and Hermann (Ber. deut. pharm. Ges., 1912, 22, 96), who considered the main product, m. p. 185°, to be 5 : 5-diethylhydantoin. This substance, prepared according to those authors, melted when pure at 198° and was, moreover, identical with a product invariably obtained in experiments involving the condensation of adalin in alkaline solution and also from the condensation, if not adequately controlled, of α-bromo-α-ethylbutyryl bromide and carbamide. 5 : 5-Diethylhydantoin

(Errara, *Gazzetta*, 1896, **26**, i, 207; Ingold, Sako, and Thorpe, J., 1922, **121**, 1193) has m. p. 165° and is readily converted by dilute alkali into a salt of diethylhydantoic acid; under the same conditions the substance, m. p. 198°, remains unchanged.

After the reaction between 2N-sodium hydroxide (rather more than 1 mol.) and α-bromo-α-ethylbutyrylcarbamide, three main products were isolated : the substance, m. p. 198°; an unsaturated acid oil, b. p. 200—210°/760 mm., which was shown to be a mixture of the isomeric forms of α-ethylcrotonic acid; and a saturated acid, b. p. 283—286°/760 mm., which corresponded in properties with the oil to which Rosenmund and Hermann ascribed the formula $C_{13}H_{20}O_6N_2$. No evidence of the formation of diethyl-hydantoin nor of the unsaturated substance, m. p. 91°, described by these authors as α-ethylcrotonylcarbamide, could be obtained.

Analysis of the substance m. p. 198° gave figures in satisfactory agreement with the formula $C_7H_{12}O_2N_2$ and, although it did not readily decolorise solutions of bromine (whilst in common with adalin it is readily oxidised by alkaline permanganate), its behaviour on hydrolysis showed clearly that it must be regarded as a ureide of α-ethylcrotonic acid (I). Hydrolysis by alcoholic potash led to the formation of an unsaturated neutral substance, m. p. 118°, and to a mixture of the two α-ethylcrotonic acids. Analysis and further hydrolysis by prolonged boiling with 20% caustic soda solution indicated that the neutral substance was an amide of α-ethylcrotonic acid (II). That this was actually the case was proved by its synthesis from α-ethylcrotonyl chloride and ammonia.

The action of α-ethylcrotonyl chloride on carbamide, or of phosphoryl chloride on a mixture of either of the forms of α-ethyl-crotonic acid and carbamide, yielded an isomeric unsaturated ureide, m. p. 158°, which showed no readiness to decolorise bromine solutions and on hydrolysis gave the unsaturated amide, m. p. 118°, together with the solid form of α-ethylcrotonic acid. The ureides, m. p. 198° and 158° respectively, are therefore probably geometrical isomerides of the unsaturated ureide (I).

Small amounts of the lower-melting isomeride and of an isomeric α-ethylcrotonamide, m. p. 104°, were also isolated from the treat-ment of α-bromo-α-ethylbutyrylcarbamide with alkali. This amide was also obtained, in better yield, by the action of excess (2 mols.) of caustic alkali and was remarkably stable when heated with moderately strong alkali, but on prolonged hydrolysis with very concentrated aqueous caustic soda it gave only ammonia and a mixture of the isomeric α-ethylcrotonic acids. It is identical with the amide, m. p. 99°, obtained by Mannich and Zernik (*Arch. Pharm.*, 1908, **246**, 183) by the action of water on α-bromo-α-ethyl-

butyramide (neuronal); a preparation thus made also melted at 104° (corr.).*

The behaviour of the amides and ureides on reduction was in harmony with the view taken of them as pairs of isomerides of unsaturated character. The amides, m. p. 118° and 104° respectively, yielded, on reduction with sodium amalgam and water, α-ethylbutyramide, m. p. 112°, whilst the ureides, m. p. 198° and 158° respectively, reduced with sodium and alcohol, gave α-ethylbutyrylcarbamide, m. p. 207°.

The two amides, unlike the ureides, readily decolorised solutions of bromine; on treatment with bromine in carbon disulphide, that of m. p. 104° yielded a dibromide, m. p. 128°, identical with that recorded by Mannich and Zernik (*loc. cit.*), whilst the amide, m. p. 118°, gave an isomeric αβ-dibromo-α-ethylbutyramide, $CHMeBr\cdot CBrEt\cdot CO\cdot NH_2$, m. p. 79°.

The corresponding ureides, although brominated with difficulty, yielded under suitable conditions dibromides, m. p. 143° and 112° respectively, presumably racemic forms of αβ-dibromo-α-ethylbutyrylcarbamide, $CHMeBr\cdot CBrEt\cdot CO\cdot NH\cdot CO\cdot NH_2$. Although the unsaturated amides react additively with bromine far more readily than the corresponding ureides, the addition of the elements of hydrogen bromide to the former has so far not been achieved. The transformation of the more fusible to the less fusible amide is, however, brought about by treatment with hydrobromic acid, as it is also by concentrated alkali or by heat. On the other hand, the higher-melting ureide is apparently the labile form, since it is converted into that of lower melting point by boiling with hydrobromic acid. From either isomeride a small yield of β-bromo-α-ethylbutyrylcarbamide, $CHMeBr\cdot CHEt\cdot CO\cdot NH\cdot CO\cdot NH_2$, m. p. 179°, is obtained by the action of the same reagent. The product is of some interest as an isomeride of adalin.

The relationships of the ureides and amides to one another and to the isomeric α-ethylcrotonic acids are tabulated on p. 298. The stable forms of ureide, amide, and acid, alone are obtained from the acid chloride (compare Blaise and Bagard, *Ann. Chim.*, 1907, [viii], **11**, 129) and the labile forms of ureide and amide, on hydrolysis with concentrated alkali, yield the liquid form of α-ethylcrotonic acid slightly contaminated with the stable form, whereas the isomerides yield the stable form alone.

* Recently, Auwers (*Annalen*, 1923, **432**, 77) has described the preparation of an amide of α-ethylcrotonic acid, m. p. 114—115°, from α-ethylcrotonyl chloride and ammonia in ethereal solution. He was, however, apparently unable to isolate the lower-melting amide by the method of Mannich and Zernik, the amide, m. p. 114—115°, being alone obtained.

Labile forms.   Stable forms.

(I.) CHMe:CEt·CO·NH·CO·NH₂   CHMe:CEt·CO·NH·CO·NH₂
  α-Ethylcrotonylcarbamide,   HBr   α-Ethylcrotonylcarbamide,
        m. p. 198°.   ——→   m. p. 158°.

N-KOH

  CHMe:CEt·CO·NH₂   (II. CHMe:CEt·CO·NH₂   CHMe:CEt·COCl
  α-Ethylcrotonamide, HBr, heat α-Ethylcrotonamide,   NH₂   α-Ethyl-
    m. p. 104°.   ————→   m. p. 118°.   ←——   crotonyl
                  or con-   chloride.
                  centrated
                  alkali

                              20%   H₂O
                              NaOH   PCl₃

CHMe:CEt·CO₂H   CHMe:CEt·CO₂H
Liquid α-ethyl-   HBr or PCl₃   Solid α-ethylcrotonic acid,
crotonic acid,   m. p. 42°.
  b. p. 199°.

The acid oil, b. p. 283—286°, to which Rosenmund and Hermann ascribed the formula $C_{13}H_{20}O_6N_2$, solidified on standing in the ice-chest and then had m. p. 24°. Analysis gave no figures in satisfactory agreement with a simple formula, but the substance, which behaved as a dibasic acid, gave, on hydrolysis, diethylglycollamide, OH·CEt₂·CO·NH₂, m. p. 88°, and diethylglycollic acid, OH·CEt₂·CO₂H, m. p. 79—80°, and was thus recognised as the symmetrical bisdiethylglycollylcarbamide, (OH·CEt₂·CO·NH)₂CO, described by Clemmensen and Heitman (*Amer. Chem. J.*, 1908, 40, 287); when purified essentially by their method, it had m. p. 29° and corresponded with the formula $C_{13}H_{24}O_5N_2$. Its silver salt reacted with ethyl iodide to produce *bis-α-ethoxy-α-ethylbutyrylcarbamide*, (OEt·CEt₂·CO·NH)₂CO, b. p. 240°, which gave, on hydrolysis, *α-ethoxy-α-ethylbutyramide*, m. p. 36°.

The presence of alkali cyanide in the reaction mixture from the action of caustic alkali on α-bromo-α-ethylbutyrylcarbamide, noted by Rosenmund and Hermann and confirmed by the present author, is probably to be accounted for by the intermediate formation of a small amount of α-bromo-α-ethylbutyramide. The latter was shown by Mannich and Zernik (*loc. cit.*) to give, on treatment with caustic soda, diethyl ketone and hydrobromic and hydrocyanic acids (compare also Mossler, *Monatsh.*, 1908, 29, 69). The amount of diethyl ketone isolated, as semicarbazone from the main reaction mixture, was in approximate agreement with that required by the assumption that sodium cyanide had been formed in equimolecular quantity.

Treatment of α-bromo-α-ethylbutyrylcarbamide and the α-ethylcrotonylcarbamides with N- or 2N-alkali always led to the pro-

duction of larger quantities of the mixed α-ethylcrotonic acids than would be expected on the assumption that the corresponding amides are necessarily intermediate products of the hydrolysis. It seems probable, therefore, since under similar conditions of time, concentration of alkali, etc., the unsaturated amides are not appreciably hydrolysed to the corresponding acids, that the hydrolysis of the unsaturated ureides proceeds in two directions :—

(a) $CHMe{:}CEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2O \longrightarrow CHMe{:}CEt{\cdot}CO_2H + NH_2{\cdot}CO{\cdot}NH_2.$

(b) $CHMe{:}CEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 + H_2O \longrightarrow CHMe{:}CEt{\cdot}CO{\cdot}NH_2 + NH_3 + CO_2.$
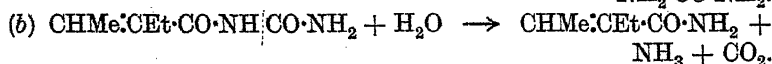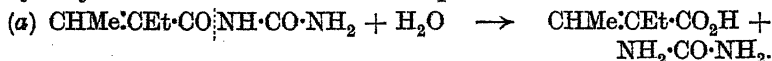
Under certain conditions, the carbamide formed in the action (a) escapes complete hydrolysis to ammonia and carbon dioxide and can be isolated in part as the characteristic nitrate.

Bisdiethylglycollylcarbamide, on the other hand, was hydrolysed by mild treatment with alkali to the stable amide, and only further to diethylglycollic acid under the more drastic conditions necessary to hydrolyse the amide.

Finally, the small amount of the stable form of α-ethylcrotonyl-carbamide isolated from the action of 2N-caustic soda solution on adalin appears to be derived directly from the latter by the elimination of hydrogen bromide, and not by the isomerisation of its labile isomeride, since no conversion of the latter on treatment with alkali of this concentration could be detected.

$CEt_2Br{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$
α-Bromo-α-ethylbutyrylcarbamide, m. p. 119°.

$CHMe{:}CEt{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$
Labile
α-ethylcrotonylcarbamide,
m. p. 198°.

Stable
α-Ethylcrotonylcarbamide,
m. p. 158°.

$2[OH{\cdot}CEt_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2]$
(Not isolated)

$[CEt_2Br{\cdot}CO{\cdot}NH_2]$
α-Bromo-α-ethyl-butyramide.

$CHMe{:}CEt{\cdot}CO{\cdot}NH_2 + NH_3 + CO_2$
Labile
α-ethylcrotonamide, m. p. 104°.

$CHMe{:}CEt{\cdot}CO_2H + NH_2{\cdot}CO{\cdot}NH_2.$
Labile
α-ethylcrotonic acid,
b. p. 199°.

$OH{\cdot}CEt_2{\cdot}CO{\cdot}NH$
$OH{\cdot}CEt_2{\cdot}CO{\cdot}NH$ CO
$+ NH_2{\cdot}CO{\cdot}NH_2$
s-Bisdiethylglycollyl-carbamide, m. p. 29°.

$Et_2CO + HBr + HCN.$
Diethyl ketone.

$\longrightarrow$ α-ethylcrotonic acid, m. p. 42°.
Stable

EXPERIMENTAL.

Action of Sodium Hydroxide (1 *mol.*) *on α-Bromo-α-ethylbutyryl-carbamide.*—Commercial adalin of m. p. 119° (100 g.) was treated

with gently boiling 2N-sodium hydroxide (270 c.c.; rather more than 1 equiv.) in an apparatus through which a current of air could be aspirated and passed in sequence through sufficient of a hot 2N-solution of sulphuric acid to absorb the evolved ammonia, a strong solution of semicarbazide hydrochloride saturated with sodium acetate, and, finally, a little dilute permanganate solution acidified with sulphuric acid. A semicarbazone (a) shortly began to separate and as long as there was sufficient excess of semicarbazide there was no appreciable decoloration of the permanganate. After being heated for an hour, the mixture was cooled, the crystalline solid (b) filtered off, and the filtrate made up to 500 c.c. Fifty c.c. (c) were removed for the titration of cyanide and the remainder was extracted once with chloroform (d). The liquors were then saturated with sodium chloride, exhaustively extracted with chloroform (e), and acidified (congo-red) with concentrated hydrochloric acid, there being considerable disengagement of carbon dioxide and the liberation of an oily layer, which was completely extracted with ether (f) Finally, the mixture was neutralised exactly with caustic soda (phenolphthalein), evaporated to dryness, and the residual salt extracted in a Soxhlet apparatus successively with alcohol and acetone (g).

The semicarbazone (a), after being washed with a little water, dried (0·2 g.; m. p. 135—136°), and recrystallised from acetone, melted at 139°, alone or mixed with synthetic diethyl ketone semicarbazone. The solid (b) weighed 20 g. and after repeated crystallisation from alcohol and from acetone melted at 198° (corr.) (Found: C = 53·7; H = 7·7; N = 18·1. $C_7H_{12}O_2N_2$ requires C = 53·8; H = 7·7; N = 18·0%). This α-ethylcrotonylcarbamide crystallises from much alcohol, acetone, or benzene in long, colourless needles, is very slightly soluble in ether, and is soluble in strong alkali or strong mineral acid, from which it is thrown out unchanged on dilution or neutralisation.

The cyanide content (estimated by the Denigès method) of (c) indicated a total amount of 0·08 g. of sodium cyanide (molecular equivalence with 0·23 g. of diethyl ketone semicarbazone). The chloroform extract (d), dried over anhydrous sodium sulphate, left on evaporation an oil (2·5 g.) which quickly solidified and, after repeated crystallisation from alcohol, gave colourless needles, m. p. 158°, of the low-melting α-ethylcrotonylcarbamide. The further chloroform extracts (e) also left an oil which quickly solidified and, after repeated crystallisation from ether, furnished about 1 g. of α-ethylcrotonamide, m. p. 104°. The ethereal extract (f), dried over calcium chloride, yielded an oil which on fractionation gave (i) an unsaturated acid oil, b. p. 200—220° (4·7 g.), and (ii) a

saturated acid fraction, b. p. 282—284° (28·2 g.). The former was identified as a mixture of the two forms of α-ethylcrotonic acid and was converted by a drop of concentrated hydrobromic acid or by the successive action of phosphorus trichloride and water into the solid form of the acid, m. p. 42°, not depressed by admixture with a genuine specimen. The examination of the fraction (ii) is described below. The combined extracts (g) yielded on evaporation no appreciable residue. The yields of the various products together accounted for practically the whole of the adalin employed.

Hydrolysis of High-melting α-Ethylcrotonylcarbamide.—(a) The ureide, m. p. 198° (40 g.) and potassium hydroxide (40 g., dissolved in the minimum of water and diluted with alcohol, 200 c.c.) were heated under reflux for 24 hours. After removal of the excess of alcohol in a vacuum, two layers formed; the upper quickly crystallised and yielded, on being drained, 2·7 g. of crude amide. The liquors yielded to ether 8·5 g. of yellow oil, which gave a further crop of crude amide somewhat contaminated with the lower-melting isomeride. The aqueous liquors, on acidification and ether extraction, gave an unsaturated acid oil (15·5 g.) which, on distillation, gave a fraction, b. p. 195—205° (6·4 g.), and a fraction, b. p. 205—220° (5·0 g.). Both showed marked unsaturation, but neither solidified on cooling. Both, however, yielded α-ethyl-crotonic acid, m. p. 42°, on treatment with phosphorus trichloride and subsequently with water.

(b) The ureide, m. p. 198° (17 g.) was heated for 1 hour on the water-bath with N-potassium hydroxide (350 c.c.). The solution was saturated with sodium chloride, filtered from a little unchanged material, and repeatedly extracted with chloroform; this removed an oil (7 g.) from which was isolated α-ethylcrotonamide, white needles, m. p. 104°. Acidification of the aqueous liquors yielded an unsaturated acid oil (4·3 g.) which, on distillation, gave nearly pure liquid α-ethylcrotonic acid, b. p. 190—200°; this was converted as before into the solid isomeride, m. p. 42°. The combined yields accounted for 95% of the unsaturated ureide employed.

(c) In a further experiment, the hydrolysis was carried on for 30 minutes only. The final liquors after removal of the neutral and the acid fraction were evaporated to dryness in a vacuum; from the residue boiling alcohol extracted carbamide (identified as the nitrate).

High-melting α-Ethylcrotonamide.—The crude unsaturated amide from the above preparation (a), on repeated crystallisation from ether, formed colourless needles or leaflets, m. p. 118° (corr.) (Found : C = 63·8;   H = 10·0;   N = 12·4. $C_6H_{11}ON$ requires

C = 63·7; H = 9·7; N = 12·4%). It is very soluble in alcohol, moderately soluble in benzene or water, slightly soluble in cold ether, and insoluble in light petroleum. Prepared synthetically from α-ethylcrotonyl chloride and strong aqueous ammonia, the same amide was obtained in 75% yield in glistening plates, m. p. 118° (Found : N = 12·5%).

Hydrolysis of High-melting α-Ethylcrotonamide.—The unsaturated amide (6·5 g.) was refluxed for 3 hours with 20% aqueous caustic soda (15 c.c.). Ammonia was evolved and, after the extraction of some 3 g. of unchanged amide by chloroform, acidification and ether extraction yielded an acid oil (3 g.), from which α-ethylcrotonic acid was obtained; m. p. 40°.

Action of Sodium Hydroxide (2 mols.) on α-Bromo-α-ethylbutyrylcarbamide.—Finely-powdered commercial adalin (100 g.) was heated under reflux with N-sodium hydroxide (1000 c.c.) for 90 minutes and, when cold, the liquid was saturated with sodium chloride, filtered from high-melting α-ethylcrotonylcarbamide (4 g.), and extracted with ether. From the extract, dried over anhydrous sodium sulphate, were obtained 4 g. of a substance which readily sublimed at about 100°, quickly solidified on cooling, and after repeated crystallisation from ether, melted at 104°, alone or mixed with α-ethylcrotonamide (m. p. 104° after several crystallisations), prepared according to Mannich and Zernik (*loc. cit.*).

Low-melting α-ethylcrotonamide crystallises in colourless needles from ether, in which it is more soluble than the high-melting isomeride, is very soluble in alcohol or chloroform, moderately soluble in benzene or water, and insoluble in light petroleum (Found : C = 63·6; H = 9·9; N = 12·5. Calc. for $C_6H_{11}ON$, C = 63·7; H = 9·7; N = 12·4%).

On acidification, the reaction product also yielded a mixture of the two α-ethylcrotonic acids, b. p. 190—220° (11 g.), and the saturated acid oil, b. p. 284—287° (26 g.).

Hydrolysis of Low-melting α-Ethylcrotonamide.—(a) α-Ethylcrotonamide, m. p. 104° (6 g.) was heated on the steam-bath for 1 hour with N-caustic potash (125 c.c.). Saturation with sodium chloride and chloroform extraction yielded the unchanged amide (5·8 g.; 97% recovery). There was no appreciable acid fraction.

(b) The amide (4 g.), boiled under reflux with 20% caustic soda (10 c.c.) for 3 hours, yielded, as before, 3 g. of unsaturated amide m. p. 100° (indefinite), which was probably a mixture of the two isomeric amides, since repeated crystallisation from ether yielded the less soluble form, m. p. 118°. The acid fraction yielded liquid α-ethylcrotonic acid (0·7 g.), b. p. 200°.

(c) The amide (3·5 g.), heated for 5 hours with boiling 40%

caustic soda (20 c.c.), yielded, when worked up in a similar way, the high-melting form of the amide (0·25 g.), together with a mixture of the two α-ethylcrotonic acids, b. p. 195—205° (3 g.).

Synthesis of Low-melting α-Ethylcrotonylcarbamide.—α-Bromo-α-ethylbutyryl bromide (200 g.; b. p. 128°/30 mm.) was run slowly into a boiling solution of potassium hydroxide (400 g.) in water (250 c.c.) and alcohol (750 c.c.). Much heat was developed and the alcohol kept boiling vigorously. The mixture was heated for 30 minutes on the steam-bath, water added to dissolve the separated potassium bromide, and the excess of alcohol removed in a vacuum. Acidification with hydrochloric acid and ether extraction yielded a mixture of the two forms of α-ethylcrotonic acid (75 g.; b. p. 190—210; yield 90% of theory). (*a*) To the mixed acids (5 g.) was added phosphoryl chloride (3 g.), followed almost immediately by 8 g. of carbamide. A vigorous reaction ensued which was not controlled and, after 30 minutes' heating on the water-bath, addition of water, and a short period of further heating, the mixture was cooled and the crude carbamide (3·5 g.) filtered off. (*b*) α-Ethylcrotonyl chloride (2·2 g.; b. p. 58°/14 mm.), prepared from the mixed acids and phosphorus trichloride, was heated on the water-bath for 2 hours with carbamide (2·5 g.). The semi-liquid mass became more viscous and was finally nearly solid. Water was added and the crude carbamide (2 g.) filtered off.

Low-melting α-Ethylcrotonylcarbamide, m. p. 158° (corr.) crystallised in colourless needles from alcohol; it was not readily soluble in cold alcohol, benzene, acetone, or ether, and did not readily decolorise bromine water (Found : C = 53·6; H = 7·8; N = 18·1. $C_7H_{12}O_2N_2$ requires C = 53·8; H = 7·7; N = 18·0%).

Hydrolysis of Low-melting α-Ethylcrotonylcarbamide.—The hydrolysis of the ureide, m. p. 158° (5 g.) was effected with N-caustic potash (100 c.c.) under exactly similar conditions to those employed for the hydrolysis of the isomeric ureide, m. p. 198°. The chloroform extract yielded an oil (2 g.) which quickly solidified and crystallised from ether in leaflets, m. p. 118°, alone or mixed with synthetic α-ethylcrotonamide. The aqueous liquors after acidification yielded to ether an oil (1·8 g.) which quickly solidified and proved to be solid α-ethylcrotonic acid, m. p. 42°. Hydrolysis for 3 hours with concentrated alcoholic potash yielded the same products.

Reduction of the Isomeric α-Ethylcrotonamides.—A warm solution of α-ethylcrotonamide, m. p. 118° (1 g.) in water (50 c.c.), was reduced with 4% sodium amalgam (50 g.), and, after filtration from mercury, was extracted with chloroform. Desiccation and evaporation of the solvent yielded an oil which solidified on stand-

ing. Repeated crystallisation from ether yielded white needles, m. p. 111°, which did not reduce alkaline permanganate or decolorise bromine water. α-Ethylcrotonamide, m. p. 104°, under the same conditions, yielded the same product.

α-Ethylbutyramide.—α-Ethylbutyryl chloride, b. p. 65°/70 mm. (5 g.), was run slowly with continuous stirring into excess (10 c.c.) of concentrated ammonia solution cooled by ice. The solid which separated, together with a further quantity obtained by chloroform extraction (3·5 g. in all; 82% of theory), crystallised from ether in colourless needles, m. p. 112° (corr.), alone or mixed with the reduction product from either α-ethylcrotonamide (Found : N = 12·3. Calc. for $C_6H_{13}ON$, N = 12·2%). The alkaline hydrolysis of synthetic α-ethylbutyrylcarbamide likewise led to the same saturated amide, m. p. 112° (E. Fischer and Dilthey, *Ber.*, 1902, **35**, 853, give m. p. 107°).

Reduction of the Isomeric α-Ethylcrotonylcarbamides.—Either isomeride (1 g.) was reduced with boiling ethyl alcohol (20 c.c.) and sodium (1·5 g.). Chloroform (50 c.c.) was added to the mixture, followed by water (100 c.c.). The solid (0·4 g.) isolated from the chloroform extract crystallised from alcohol in colourless needles, m. p. 205—206°, which did not reduce a cold alkaline permanganate solution nor depress the m. p. (206—207°) of synthetic α-ethylbutyrylcarbamide.

Bromination of Low-melting α-Ethylcrotonamide.—α-Ethylcrotonamide, m. p. 104° (2·5 g.), suspended in carbon disulphide (30—40 c.c.) at 0°, required the theoretical quantity of bromine in the same solvent to give a permanent coloration after an hour. The crystals, which began to separate during the addition, were washed with carbon disulphide, dried (3·5 g.; 58% of theory), and recrystallised from alcohol, high-melting αβ-dibromo-α-ethylbutyramide separating in colourless needles, m. p. 127—128°, slightly soluble in cold carbon disulphide, ether or petroleum (Found : Br = 58·6. Calc. for $C_6H_{11}ONBr_2$, Br = 58·6%).

Bromination of High-melting α-Ethylcrotonamide.—α-Ethylcrotonamide, m. p. 118° (2·5 g.), treated in a similar way, gave a less sharp end-point, absorption of bromine being less rapid and only towards the end of the addition was there any separation of the dibromide. The solvent was evaporated, the residue, which solidified after some hours at 0°, was washed with ether–petroleum (b. p. 40—60°), and crystallised from the same mixture, yielding low-melting αβ-dibromo-α-ethylbutyramide (2·5 g.; 42% of theory) as a slightly yellow, crystalline powder, m. p. 77—78°; by repeated crystallisation, colourless plates, m. p. 79—80°, were obtained. This dibromide was more soluble in carbon disulphide, alcohol, or

ether than the high-melting isomeride, and was somewhat soluble in hot petroleum (b. p. 40—60°) (Found : Br = 58·5.　$C_6H_{11}ONBr_2$ requires Br = 58·6%).

Bromination of Low-melting α-Ethylcrotonylcarbamide.—α-Ethylcrotonylcarbamide, m. p. 158° (5 g.) was exposed for 48 hours over excess of bromine in a closed desiccator.　Excess of bromine was removed in a current of air, and the residue refluxed with ether (200 c.c.).　After filtration, the ethereal solution was concentrated to 20 c.c., and the crystals (3 g.) which separated were recrystallised from alcohol, when low-melting α*β-dibromo-α-ethylbutyrylcarbamide* was obtained in colourless needles, m. p. 112° (Found : Br = 50·7.　$C_7H_{12}O_2N_2Br_2$ requires Br = 50·6%).

Bromination of High-melting α-Ethylcrotonylcarbamide.—The ureide, m. p. 198° (5 g.), brominated in a similar manner, gave high-melting α*β-dibromo-α-ethylbutyrylcarbamide* (3·2 g.), which crystallised from alcohol in colourless prisms, m. p. 142—143°. It is moderately soluble in ether (Found : Br = 50·4.　$C_7H_{12}O_2N_2Br_2$ requires Br = 50·6 %).

Action of Hydrogen Bromide on Low-melting α-Ethylcrotonamide.— α-Ethylcrotonamide, m. p. 104° (2·5 g.) was heated on the waterbath for 2 hours with acetic acid saturated with hydrogen bromide at 0° (25 c.c.).　Excess of the acids was removed in a vacuum, the residue (10 c.c.) nearly neutralised with 2*N*-sodium hydroxide, and the mixture extracted with chloroform.　The solid (0·6 g.) which remained after the removal of the solvent, crystallised from ether in leaflets, m. p. 117—118°, not depressed by admixture with the synthetic amide, m. p. 118°.

Behaviour of Hydrogen Bromide with High-melting α-Ethylcrotonamide.—The amide, m. p. 118° (0·3 g.) was heated for 6 hours in a sealed tube at 100° with acetic acid saturated with hydrogen bromide at 0° (2 c.c.).　The mixture, after dilution and neutralisation, gave, on extraction, only the unchanged amide, m. p. 118°.

Action of Hydrogen Bromide on Low-melting α-Ethylcrotonylcarbamide.—A mixture of the ureide, m. p. 158° (4 g.), with acetic acid saturated with hydrogen bromide at 0° (40 c.c.) was heated under reflux for 20 hours on the steam-bath and when poured into cold water (500 c.c.) yielded a solid product (1 g.).

β-*Bromo-α-ethylbutyrylcarbamide* was obtained in colourless needles, m. p. 179—180°, by repeated crystallisation from alcohol. It is sparingly soluble in alcohol, benzene, or ether (Found : N = 11·9; Br = 33·4.　$C_7H_{13}O_2N_2$ Br requires N = 11·8; Br = 33·75%).

Action of Hydrogen Bromide on Low-melting α-Ethylcrotonylcarbamide.—The ureide, m. p. 198° (5 g.) together with saturated acetic-hydrobromic acid (30 c.c.) was heated for 8 hours in a sealed

bottle in a boiling-water bath. The mixture was filtered from a little ammonium bromide, water added, and the solution nearly neutralised with 20% caustic soda solution. On cooling, a white solid (4 g.) separated, which, after repeated crystallisation from alcohol, melted at 177° and was identical with the β-bromo-α-ethyl-butyrylcarbamide described above. Chloroform extraction of the still slightly acid mother-liquors yielded a small amount of oil, which solidified on standing and after repeated crystallisation from alcohol had m. p. 158°, not depressed by admixture with the unsaturated ureide of that melting point.

Examination of the Saturated Acid, b. p. 283—286°.—Bisdiethylglycollylcarbamide was obtained in a pure condition from the acid oil, b. p. 283—286°, by a slight modification of the method proposed by Clemmensen and Heitman (*loc. cit.*) involving the preparation of the silver salt from the ammonium salt, followed by the decomposition of the former by hydrogen sulphide. It then melted at 29° and agreed in physical and chemical properties with bisdiethylglycollylcarbamide prepared synthetically (Found : C = 54·1, 54·0; H = 8·1, 8·3; N = 9·8, 9·7. Calc. for $C_{13}H_{24}O_5N_2$, C = 54·1; H = 8·3; N = 9·7%).

Hydrolysis of Bisdiethylglycollylcarbamide.—(a) The oil, b. p. 283—286° (21 g.) was refluxed for 48 hours on the steam-bath with alcoholic potash from potassium hydroxide (21 g.) dissolved in the minimum of water and 100 c.c. of alcohol. Ammonia was evolved during the whole period of heating. The mixture yielded on dilution and ether extraction an oil, b. p. 164°/25 mm. (10 g.). This quickly solidified and on crystallisation from ether gave diethylglycollamide, m. p. 88°, in colourless, hexagonal plates (Found : N = 10·8. $C_6H_{13}O_2N$ requires N = 10·7%). The aqueous liquors on acidification likewise yielded an acid fraction (10 g.) which, on distillation, boiled for the most part at 115—130°/10 mm. There was a small amount of unchanged material b. p. 152—155°/10 mm. The main fraction quickly solidified and crystallised from petroleum (b. p. 60—80°) in colourless needles, m. p. 80°, not depressed by admixture with synthetic diethyl-glycollic acid, m. p. 81°. (b) The same oil (40 g.), hydrolysed under the same conditions for 3 hours only, yielded diethylglycollamide (15 g.) and unchanged material (10 g.). No diethylglycollic acid could be isolated. (c) The oil (13 g.), boiled on the sand-bath for 1 hour with 2*N*-caustic soda, gave no diethylglycollamide, and the acid fraction yielded only unchanged material (12·5 g.).

Bis-α-ethoxy-α-ethylbutyrylcarbamide.—The silver salt (19 g.) of bis-diethylglycollylcarbamide (Found : Ag=40·1. $C_{13}H_{22}O_5N_2Ag_2,2H_2O$ requires Ag = 40·1%) from the saturated acid oil, b. p. 283—286°,

after being dried at 100°, was heated with ethyl iodide (25 c.c.) for 15 minutes, silver iodide was removed by filtration, and the oil (12 g.; 97% of theory), which was insoluble in caustic soda, distilled at 160—170°/60 mm. The oil so obtained had a characteristic odour of garlic and b. p. 240° (Found : C = 59·0; H = 9·3. $C_{17}H_{32}O_5N_2$ requires C = 59·3; H = 9·3%). A preparation in a similar way from synthetic bisdiethylglycollylcarbamide yielded the same product.

Hydrolysis of Bis-α-ethoxy-α-ethylbutyrylcarbamide.—The ethoxy-carbamide (20 g.) was hydrolysed for 12 hours on the steam-bath with alcoholic potash from potassium hydroxide (20 g.) in the minimum of water and 200 c.c. of alcohol. After the removal of excess alcohol in a vacuum and dilution, ether extraction gave an oil (10 g.), b. p. 141—144°/11 mm., which solidified after remaining a few hours at 0°.

α-Ethoxy-α-ethylbutyramide, when pure, melts at 36° and is very soluble in most organic solvents, but practically insoluble in light petroleum. It could not be crystallised satisfactorily and was apparently best purified by repeated distillation in a vacuum (Found : N = 8·7. $C_8H_{17}O_2N$ requires N = 8·8%). The aqueous liquors from this preparation yielded practically no acid fraction, and ethoxyethylbutyramide was found to be extremely resistant to the hydrolytic action of alkali.

XLVIII.—*The Direct Combination of Ethylenic Hydrocarbons with Hydrogen Sulphites.*

By ISRAEL KOLKER and ARTHUR LAPWORTH.

AGENTS, such as ozone, which attack the simplest compounds, have been distinguished (as " Class I ") by Lapworth and McRae (J., 1922, **121**, 2741; compare also Lapworth, *Mem. Manchester Phil. Soc.,* 1920, **64**, iii, 11) from others (" Class II "), which

are inert towards ethylenic hydrocarbons but which nevertheless are additive to the ethylenic group when the latter occurs in the α-position with respect to a carbonyl, cyano, or similar group.

It is significant that all the known agents of the second class are either (IIa) metallo-compounds or (IIb) compounds of the general type, H–Z, in which the hydrogen atom is capable of being replaced by the action of metals.

Examples of sub-class IIa are Grignard reagents, potassium cyanide, and sodio-derivatives of ketones, esters and nitriles. Examples of IIb are HCN, $HCH(CO_2Et)_2$, HNR_1R_2, the last including amines, hydroxylamines, and hydrazines. The electronic theory of metallic compounds suggests that the radical of each agent of class IIa is capable of existence in all cases as a negatively charged ion, $Z-$. In some cases the free ion $Z-$ is identical in constitution with the radical as it occurs in the compound H–Z (example: H–NH_2); in other cases, it is probably not; (example: H–$CH_2 \cdot NO_2$), but the structural difference is such that intraconversion readily takes place in either direction. As is well known, agents of sub-class IIb also form addition products with many saturated carbonyl compounds.

Not all compounds which have the characters defined in the preceding paragraph can be referred to Class IIb; thus, powerful acids are by definition excluded from this class, as they attack ethylenic compounds of all types.

It is further necessary to observe that in referring any agent to Class IIb there are restrictions as to the experimental conditions prevailing while the agent is applied. For example, hydrogen cyanide may properly be referred to Class IIb when applied in presence of an alkaline catalyst, but not in presence of an acid catalyst unless it has been shown that under the same conditions the combination is inert or nearly so toward ethylenic hydrocarbons.

Within the range occupied by IIb, which must be limited at one extreme by acids too weak to attack ethylenic compounds at measurable speed and at the other extreme by very feebly ionisable compounds, such as ammonia, there does not at present appear to be any direct relation between the additive efficiency of the agent and the electro-affinity of the anion. Thus many very weak acids appear almost or quite unable to form stable addition products with carbonyl compounds.

With reference to Class II as a whole, it is probably true that no compounds of which the ion $Z-$ has a very high affinity for the charge can be included in either sub-class (compare Lapworth, *loc. cit.*). There are, for example, no cases recorded where the potassium or sodium salts of powerful acids form additive com-

pounds with carbonyl compounds. The powerful acids have already been excluded for the reasons above stated.

From the preceding considerations, it is clear that any agent which forms addition products with the carbonyl group of aldehydes and ketones or with the ethylenic linking in αβ-unsaturated carbonyl compounds may safely be referred to sub-group IIb only when it is known that the agent does not attack ethylenic hydrocarbons under comparable conditions; in many cases, as in the instance of ammonia, experimental evidence is already extensive and so uniformly negative, that this indifference may confidently be inferred, whilst in other cases further investigation is required.

The correct classification of agents additive to ethylenic compounds is of the utmost importance in studying the influence of atoms and groups on the properties of others in the same molecule. The authors have made a careful study of two series of agents previously referred, in the papers above specified (*loc. cit.*), to Class II.

The experiments carried out by the authors and by other workers in these laboratories on the possible addition of hydrogen cyanide and metallic cyanide to ethylenic hydrocarbons, including *cyclo*hexene and styrene, have given uniformly negative results. As the addition products in these cases would have been nitriles, easily convertible into carboxylic acids and so capable of detection even in traces, it may be concluded that metallic cyanides and hydrogen cyanide in absence of acid catalysts are indeed highly selective, and that when they do attack an ethylenic linking the latter is almost certainly affected by conditions similar to those which obtain in αβ-unsaturated ketones.

The other series of reagents tested were sulphites, and more especially hydrogen sulphites. The sole instance hitherto recorded (so far as we have been able to discover) of a hydrocarbon combining directly with hydrogen sulphites is that of styrene and even in that case the published evidence was inconclusive (Miller, *Annalen*, 1877, **189**, 340; Labbé, *Bull. Soc. chim.*, 1893, [iii], **22**, 1077; Dupont and Labaune, *Sci. Ind. Bull.*, 1912, [iii], **7**, 3). In the case of styrene, moreover, there was an element of doubt whether phenyl can exercise the same influence on a double bond as carbonyl can. Similar uncertainty existed in the theoretical interpretation of the observations of Dupont and Labaune (*loc. cit.*), who obtained additive products of hydrogen sulphites with unsaturated alcohols.

The results obtained by the present authors remove all doubt on many of these moot points. Hydrogen sulphites combine directly with ethylenic hydrocarbons, and the failure of previous investi-

gators fully to establish this fact is attributable to the unsuitable experimental conditions used.

Special precautions to ensure intimate contact between the hydrocarbons and the aqueous solutions are usually but not invariably necessary. They may consist in emulsifying with the aid of purified kieselguhr. Contrary to expectations, dilution of the sulphite solution, possibly by an effect on the solubility of the hydrocarbons, favoured the interaction.

A not less important practical feature in the later experiments was the use of ammonium hydrogen sulphite instead of the sodium or potassium salt. This device admits of the ready removal of any excess of the reagent by boiling with sufficient barium hydroxide, when insoluble barium sulphite is formed, ammonia is expelled, and such organic addition products as are not destroyed during this process are easily isolated as soluble barium salts.

Pinene, dipentene, *cyclo*hexene, crude " amylene," and even the completely symmetrical ethylene combine readily under favourable conditions with hydrogen sulphites, usually in the cold, yielding products which for the most part appear to be the salts of the expected saturated sulphonic acids ; but these are usually mixed with a variable proportion of other salts, apparently isomeric with the sulphonates. These secondary products, unlike the true sulphonic acids, are hydrolysed by dilute acids or alkalis, and are probably salts of the alkyl hydrogen sulphites, though some slight doubt attaches to this view of their constitution. These salts appear to be considerably more stable than the salts of alkyl hydrogen sulphites prepared by union of sulphur dioxide with sodium alkyloxides, but this may be due to stabilisation by the other salts present ; indeed the authors have observed (1) that the hydrolysis of the salts of methylethionic acid, $SO_3H \cdot CH(CH_3) \cdot CH_2 \cdot SO_4H$ (which normally is readily effected by dilute acids), takes place much more slowly if excess of salts of methylisethionic acid,

$$SO_3H \cdot CH(CH_3) \cdot CH_2 \cdot OH,$$
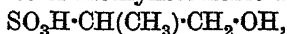
are present and (2) that pure barium methylethionate decomposes at 100°, but in presence of 9—10 times its weight of isethionate does not decompose appreciably below 150°. It is just possible, however, that two series of alkyl sulphurous acids exist.

It seems probable that carbonyl compounds react with bisulphite, as with metallic cyanide, by first capturing the anion. Ethylenic hydrocarbons evince no definite preference for anions and may react with bisulphites, either by first capturing the hydrogen ion or by uniting with the unsaturated centres of the sulphite molecules much as they unite with ozone, and possibly in both ways.

The gross result of the process of addition of hydrogen sulphites

to ethylenic hydrocarbons may thus be represented by the following scheme as adapted for sodium hydrogen sulphite :

$$CR_1R_2 \colon CR_3R_4 + NaHSO_3 \Big\langle \begin{array}{l} CHR_1R_2 \cdot CR_3R_4 \cdot SO_3Na. \\ \\ CHR_1R_2 \cdot CR_3R_4 \cdot O \cdot SO_2Na. \end{array}$$
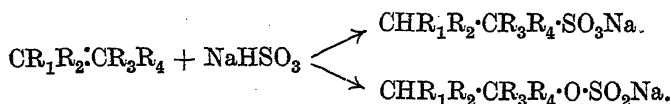
Hydrogen sulphites must now therefore be omitted from the list of reagents of Class II.

<center>EXPERIMENTAL.</center>

Throughout this section, the term " molar " and the symbol M applied to a hydrogen sulphite solution denote a solution containing one gram-molecule per litre.

Inorganic sulphite in solutions of the reaction products was assumed to be absent when mineral acids in the cold caused no evolution of sulphur dioxide and when iodine was not decolorised.

General Method of Treatment of Insoluble Fluid Compounds with Ammonium Bisulphite Solution.—Usually the fluid unsaturated compound was shaken vigorously at intervals during several days with $M/4$-ammonium hydrogen sulphite and kieselguhr. The kieselguhr was then separated by filtration, washed with boiling water, and the united filtrates were heated with excess of barium hydroxide until ammonia ceased to be evolved. The whole was then neutralised with dilute sulphuric acid, the precipitated barium sulphite and sulphate were filtered off and washed with boiling water, the filtrates being finally evaporated to dryness on the steam-bath.

Studies of the Influence of Conditions on Speed of Addition of Ammonium Bisulphite to cyclo*Hexene.*—Owing to adsorption of solutes by the kieselguhr used as emulsifying agent, it was found necessary in comparative experiments to convert the addition product into barium salt and then to isolate and weigh this.

In one series of four experiments the following results were obtained, using 5 c.c. of *cyclo*hexene in each instance with $M/4$-ammonium hydrogen sulphite solution.

	240 c.c.	480 c.c.
Volume of $M/4$-NH$_4$HSO$_3$ solution used	240 c.c.	480 c.c.
Excess of NH$_4$HSO$_3$ more than theory	25%	150%
Yield (% of theory), without kieselguhr	*16·8*	*40·0*
Yield (% of theory), with kieselguhr	*19·3*	*57·0*

In another series of three parallel experiments, using the same quantity, namely 5 c.c of *cyclo*hexene, with the same weight of ammonium bisulphite in each experiment, but dissolved in different weights of water, all with shaking at intervals during 10 days, the following results were obtained. In this series no kieselguhr was used.

Strength of bisulphite solution	$2M$	M	$M/2$
C.c. of bisulphite solution	60	120	240
Weight of crude barium salt obtained ...	1·29	1·51	2·26
Yield of crude product, % of theory ...	*10·3*	*12·1*	*18·0*

It is evident from the first series that kieselguhr has a very favourable influence on the yield, especially when a considerable excess of hydrogen sulphite is used. The two series taken in conjunction show that the yield improves with the dilution of the hydrogen sulphite at least up to $M/4$; the volumes of fluid to be evaporated, however, set a limit to the practical application of this fact.

Examination of Products from cyclo*Hexene.*—(a) *With sodium hydrogen sulphite.* When *cyclo*hexene (30 c.c.) was shaken at intervals with $M/2$-hydrogen sulphite solution (1800 c.c.) for 8 days, the resulting aqueous solution separated from unchanged *cyclo*hexene (found : 20 c.c.), evaporated to dryness, and extracted with 96—98% spirit, a white powder (1·9 g.) was obtained (Found : Na = 12·3. $C_6H_{11} \cdot SO_3Na$ requires Na = 12·3%). This powder gave no sulphuric acid when boiled with excess of dilute hydrochloric acid, and was free from inorganic sulphite; on hydrolysis with boiling sodium hydroxide, however, it yielded a little inorganic sulphite, estimated from titrations with iodine to represent 6—7·5% of sodium *cyclo*hexyl sulphite.

(b). *With ammonium hydrogen sulphite.* cyclo*Hexene (36 c.c.), $M/4$-ammonium bisulphite solution (3360 c.c.), and kieselguhr (120 g.) were shaken together at intervals during 10 days. On working up the product as on p. 311, a brown solid was obtained which on recrystallisation yielded white, hexagonal plates of barium *cyclo*hexanesulphonate, identical with that obtained, by the method of Borsche and Lange, from *cyclo*hexyl chloride through the sulphinic acid (*Ber.*, 1905, **38**, 2766) [Found : $H_2O = 13·5$; Ba (in dried salt) = 29·6. $(C_6H_{11} \cdot SO_3)_2Ba, 4H_2O$ requires $H_2O = 13·4$; Ba (in anhydrous salt) = 29·7%]. The identity was established by direct comparison of the barium salts and of the sulphanilides (m. p. 85°).*

* The following new derivatives of *cyclo*hexanesulphonic acid were prepared and examined during the course of the work. *Sodium* salt, prisms, readily soluble in water and in dilute alcohol (Found : Na = 11·1. $C_6H_{11} \cdot SO_3Na, H_2O$ requires Na = 11·3%). *Ammonium* salt, hygroscopic and exceedingly soluble in water; very readily soluble in 98% spirit, crystallising therefrom in granules. *Magnesium* salt, rhombic plates, by spontaneous evaporation of an aqueous solution. Very readily soluble in water. *Copper* salt, small, light green, rhombic plates, moderately soluble in water [Found : $H_2O = 15·4$. $(C_6H_{11} \cdot SO_3)_2Cu, 4H_2O$ requires $H_2O = 15·6\%$]. *Sulphonyl chloride*, analysed by Borsche and Lange and described by them as an oil, separates from ether in rhombic plates, m. p. 106°. *Sulphonamide*, may be crystallised from water and melts at 93—94°.

The nature of the crude brown solid product was investigated. When boiled for 4 hours with a large excess of 12% sodium hydroxide, it yielded sulphite corresponding with 2% of alkyl sulphite. When boiled with 10—15% hydrochloric acid, it did not yield any sulphate, but some sulphur dioxide was detected. When 3·5 g. were boiled for 6 hours with 15% sulphuric acid (50 c.c.), some sulphur dioxide was evolved, the solution turned light yellow in colour, and a slight aromatic odour was observed. The product of this hydrolysis could not be isolated, but after removal of constituents soluble in ether and neutralisation of the solution with barium carbonate, evaporation yielded 3·1 g. of pure barium *cyclo*hexanesulphonate. It would thus seem that the material contains at least 90% of ammonium *cyclo*hexanesulphonate together with a small quantity of an organic compound which yields sulphurous acid or sulphite on hydrolysis.* This compound could not be isolated, but it was observed that the mother-liquor remaining after separation of *cyclo*hexanesulphonate from the crude product at first gave with ferric chloride a deep red coloration similar to that obtained with sulphites and sulphinates; later, this test gave a negative result, so that the compound causing this coloration was evidently unstable, either to water or to air, or to both.

Ethylene and Ammonium Hydrogen Sulphite.—Ethylene was brought into contact with $M/4$-ammonium sulphite (2 litres) in a large bottle at about atmospheric pressure with occasional shaking. At first the solution absorbed nearly its own bulk of the gas during each interval of 24 hours, when the residual gas, with any gaseous impurities in it, was allowed to escape and was then replaced by fresh ethylene. After this process had been repeated daily during a fortnight, about 5 litres of ethylene had been absorbed and the original speed of absorption reduced by about four-fifths. The liquid was then worked up in the usual way and 13 g. of crude barium salts were obtained.

* It is difficult to reconcile the properties of this secondary constituent with the assumption that it is sodium *cyclo*hexyl sulphite, as it has resisted the operations used in preparing the crude product. For comparison, sodium *cyclo*hexyl sulphite was made by passing sulphur dioxide into (a) a solution of sodium in *cyclo*hexanol and precipitating with alcohol : (b) a suspension of sodium *cyclo*hexyl oxide in benzene and then draining the solid on porous earthenware. The solid obtained by either process was, like other salts of alkyl sulphurous acids previously described, extremely unstable, losing sulphur dioxide on exposure to air and being immediately hydrolysed in aqueous solution with liberation of inorganic sulphite (Found, in sodium *cyclo*hexyl sulphite made by process (b) : Na = 13·4. $C_6H_{11}\cdot SO_3Na$ requires Na = 12·4%. 0·346 G. dissolved in water required 39·5 c.c. of $N/10$-I_2, while one molecule of sulphite from $C_6H_{11}\cdot SO_3Na$ requires 37·2 c.c.). (For comments on these points, compare introductory section.)

The salts consist mainly of barium ethanesulphonate, but also, as in the case of *cyclo*hexene, of small quantities of other salts, which give a red coloration with ferric chloride and are somewhat stable towards alkalis but unstable towards boiling mineral acids, which cause evolution of sulphur dioxide but no liberation of sulphuric acid [Found, in barium salt : $H_2O = 9.2$; Ba (in anhydrous salt) $= 38.5$. $(C_2H_5 \cdot SO_3)_2Ba,2H_2O$ requires $H_2O = 9.2$; $(C_2H_5 \cdot SO_3)_2Ba$ requires $Ba = 38.7\%$].

The sulphonamide made from this salt was soluble in water, and easily recrystallised from ether, forming prisms, m. p. 59—60° (James, *J. pr. Chem.*, 1882, [ii], **26**, 384, gives the melting point of ethanesulphonamide as 56°).

Commercial "Amylene" and Ammonium Hydrogen Sulphite.— Combination was here so rapid that in 7 days, with occasional shaking, 5·3 c.c. of "amylene" were almost completely absorbed by $M/4$-ammonium hydrogen sulphite solution, without kieselguhr. On working up in the usual way, 9·4 g. of crude soluble barium salt (86% of theory) were obtained [Found : $Ba = 31.5$. $(C_5H_{11} \cdot SO_3)_2$ Ba requires $Ba = 31.3\%$].

The crude salt did not decolorise permanganate nor absorb bromine : it gave no sulphur dioxide or sulphuric acid when boiled for several hours with 15% hydrochloric acid, and 95% of the original product was recoverable. "Amylene" was exceptional among the hydrocarbons examined in yielding nothing but true sulphonic derivatives. As the "amylene" used was the mixture of several isomerides obtained from fusel oil, the products were not further examined.

Dipentene and Ammonium Hydrogen Sulphite.—Dipentene (15 c.c.), ammonium hydrogen sulphite ($M/4$; 2000 c.c.), and kieselguhr (50 g.), shaken at frequent intervals during 14 days, gave 12·1 g. of barium salts, at least 90% of which consist of *barium menthane-disulphonate* [Found : H_2O (lost at 160°) $= 4.0$.   •

$$C_{10}H_{18}(SO_3)_2Ba,H_2O$$

requires $H_2O = 4.0\%$. In the anhydrous salt; found $Ba = 31.4$, $S = 15.1$; theory requires $Ba = 31.6$, $S = 14.7\%$].

This salt is readily soluble in water, forms clusters of needles, and is stable to boiling mineral acid. The mother-liquors obtained on recrystallising the salt from water decolorise a little bromine or permanganate and slowly evolve some sulphur dioxide when boiled with dilute sulphuric acid.

Pinene and Ammonium Hydrogen Sulphite.—From pinene (32 c.c.), ammonium hydrogen sulphite ($M/4$; 2000 c.c.), and kieselguhr (70 g.), after 12 days, 7·4 g. of mixed soluble barium salts were isolated, but retained an odour resembling pinene after repeated

extraction with absolute alcohol. The crude product differed appreciably from that obtained from any other hydrocarbon, inasmuch as the proportion of hydrolysable salt was nearly 45% of the whole. When 2 g. were boiled with 15% sulphuric acid, much sulphur dioxide was evolved, and appreciable quantities of an oil having a terpene-like odour appeared. After removing the oil with ether, and the sulphuric acid with barium carbonate, only 1·1 g. of stable barium salt were recovered. The crude product, which was free from inorganic sulphate, also discharged the colour of an unusually large proportion of bromine.

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  THE UNIVERSITY, MANCHESTER.   [*Received, November 7th,* 1924.]

ADDENDUM.—Throughout this paper the terms " hydrogen sulphite " and " bisulphite " are used interchangeably and without regard to the question of the constitution of salts to which these names have commonly been applied in the past.

XLIX.—*A Method of Measuring the Dielectric Constants of Liquids.*

By LEONARD ALFRED SAYCE and HENRY VINCENT AIRD BRISCOE.

THE introduction of the triode valve has made possible many accurate methods for the measurement of physical constants and it has been employed by several workers in the determination of dielectric constants. Considerable accuracy has thus been attained in the measurement of dielectric constants approaching unity, *viz.*, those of the gases (Carman and Lorance, *Physical Rev.*, 1922, **20**, 715; Gill, *Radio Rev.*, 1921, **2**, 450; Wagstaff, *Phil. Mag.*, 1924, [vi], **47**, 66), but the dielectric constants of liquids which are much greater than unity have not hitherto been measured with similar accuracy (Whiddington, *Proc. Camb. Phil. Soc.*, 1921, **20**, 445; Hyslop and Carman, *Physical Rev.*, 1920, **15**, 243). This is mainly due to the difficulty of securing absolute constancy in the operation of valve-maintained circuits (Whiddington, *Engineering*, 1920, **110**, 384; Wagstaff, *loc. cit.*) and of obtaining a variable condenser combining a large range of variation with a sufficient accuracy of setting (Hyslop and Carman, *loc. cit.*). Further, in previous methods the dielectric has been stressed in a circuit directly coupled to a triode, and in such circuits, although the fundamental frequency may be known, yet the wave-form is not usually sinusoidal but may be resolved into many harmonics, some of

considerable amplitude. Possibly this is not seriously disadvantageous in work upon gases, but in the case of dielectrics in which the variation of dielectric constant with frequency is appreciable it is evident that precise measurements of this property can be made only if the applied stress be of sine wave-form.

The following method has therefore been developed in order to secure the conditions here seen to be required for the accurate measurement of relatively large dielectric constants.

General Principles.—If oscillatory currents are maintained in the circuit L_1C_2 by means of a triode connected as shown in Fig. 1, the magnitude of the direct component of the current in the anode circuit of the triode is a function of the magnitude of the oscillatory currents in L_1C_2 (Dowling, *Proc. Roy. Dublin Soc.*, 1921, **16**, 185). If, now, a second oscillatory circuit, L_3C_3, is loosely coupled to L_1C_2, little or no energy is withdrawn from the latter until the natural

<div align="center">FIG. 1.</div>
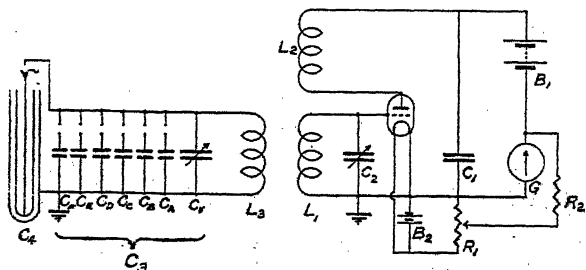
frequency of L_3C_3 approaches that of L_1C_2. Resonance between the two circuits is then shown by a sudden decrease in the direct component of anode current of the triode. If the coupling between L_1 and L_3 is sufficiently tight, the reduction in the anode current will continue throughout a considerable change of L_3C_3, for the latter circuit is forced into resonance with L_1C_2 over a considerable range of adjustment and then suddenly " breaks away " from the control of L_1C_2. The coupling between L_1 and L_3 can, however, be so adjusted that when a gradual change is made in the adjustment of C_3 the anode current steadily decreases to a minimum and thereafter steadily increases. These conditions afford an extremely sensitive null method of observing when L_3C_3 is adjusted to a given frequency, *i.e.*, the frequency of L_1C_2. If the frequencies of the two circuits are of the order of $10^6\sim$ per second, the resonance point is shown so critically that, with ordinary precautions, C_3 can be reset with an error not exceeding $0.005\mu\mu$F. If, now, another condenser, C_4, of unknown capacity, be connected in parallel with C_3, then, in order to restore resonance between the two circuits, a reduction in

the value of C_3 is necessary, such reduction being a measure of the capacity of C_4. Thus, unknown capacities can be measured accurately in terms of C_3, the frequency at which the measurement is made being that of $L_1 C_2$. The coupling between the two circuits is so loose that the stress applied to the dielectric of the unknown condenser, C_4, is very small and has a wave-form free from the distortion almost inevitable in a valve-maintained circuit. By this method the measurement of an unknown condenser involves two null galvanometer adjustments and in practice these are made within such a short time that errors due to slight variations in the frequency of $L_1 C_2$, due to variations in batteries, etc., are insignificant.

The Experimental Method.—The practical application of the above principles to the measurement of the dielectric constants of liquids presents two main problems :

(1). The construction of a condenser of fixed dimensions in which either a vacuum, air, or the substance under investigation may be used as dielectric at will. For convenience, this is hereafter called the " dielectric container."

(2). The construction of a variable condenser having the relatively wide range of $500\mu\mu F$ and yet such that it can be set and read with an error not exceeding $0 \cdot 005\mu\mu F$.

(1). The capacity of the dielectric container is measured when full of air, or evacuated, and again when full of the liquid under examination, the ratio of the latter capacity to the former being the dielectric constant of the liquid at the temperature and frequency employed. The type of condenser that has been found most suitable is shown in Fig. 2. It resembles an elongated Dewar flask and consists of two glass tubes, like large " boiling-tubes," one sealed inside the other. Access to the annular space between these tubes is given by the tubes G and H. Platinum electrodes are fused through the bottom of the inner tube and through the side of the outer tube. Both internal surfaces of the annular space are silvered to the height shown and these silver films constitute the " plates " of the condenser. It was thought advisable to thicken the silver films by several successive applications of the silvering solution. A small glass elbow-tube, J, is cemented to the outer tube where the platinum electrode pierces it, and mercury, poured into the little cup so formed, provides a means of making a connexion to the outer silver coating. A little mercury is also poured into the inner tube to cover the other platinum electrode and connexion with it is made by a long stiff wire. At the top of this wire is cemented a small glass cup containing mercury and having a little hook of glass rod fused on at one side. A stiff wire,

coming from the remainder of the apparatus, normally rests on this glass hook, but is transferred to the adjoining mercury cup in order to switch the condenser into circuit. The condenser is immersed in a thermostat so that the water-level is a few milli-metres below the top, and the thermostat and outer silver coating of the condenser are connected to the " earthed " side of the remaining apparatus.
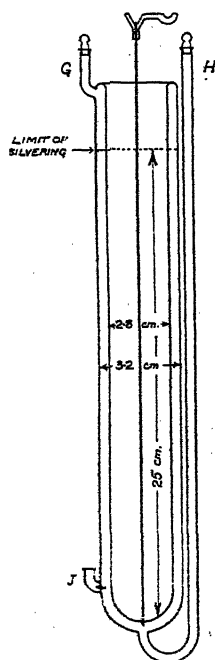
FIG. 2.   FIG. 3.
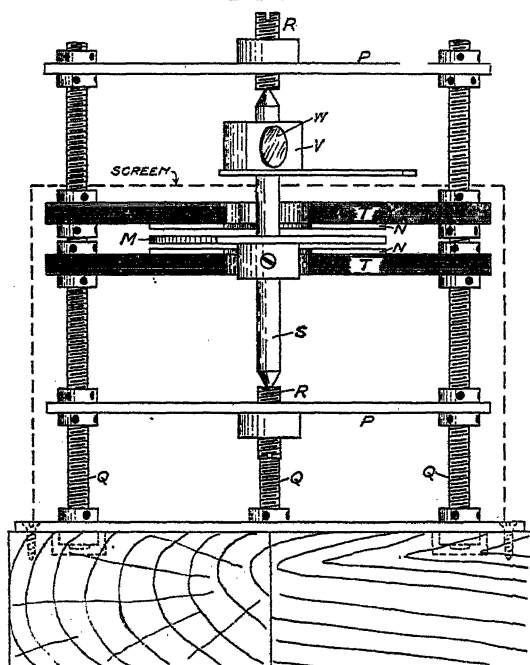
(2). The wide-range variable condenser is an assembly of six condensers of fixed capacity with a small one of variable capacity. The former are labelled from " a " to " f " and are made of the following approximate values : $C_a = 10\mu\mu F$, $C_b = 20\mu\mu F$, $C_c = 40\mu\mu F$, $C_d = 80\mu\mu F$, $C_e = 160\mu\mu F$, $C_f = 320\mu\mu F$. The small variable condenser is variable over a range of $10\mu\mu F$. It is per-manently in circuit, but any, or all, of the fixed-capacity condensers may be switched in parallel with it by means of mercury cups and bridges. Each fixed-capacity condenser is made with interleaved aluminium plates separated by air. One set of plates is connected to an earthed metal base-plate and to an earthed tin-plate screen which envelops the condenser, the other set of plates being con-nected to a brass rod which acts as the " live " terminal.

The construction of the small variable condenser is shown in Fig. 3. It consists, essentially, of a single semi-circular vane, M, free to rotate between two semi-annular rings, N. The framework of the condenser comprises two triangular brass end-plates, P, held apart by three vertical rods, Q. Each end-plate is provided with a longitudinally-drilled steel screw, R, and these two screws are the bearings for the conical ends of a rotatable spindle, S. The spindle carries a thick semi-circular brass plate, M, accurately turned on both faces whilst mounted on the spindle. The two fixed plates of the condenser are two semi-annular rings, N, made of heavy brass and accurately turned, secured respectively to two triangular ebonite platforms, T, which may be fixed at any suitable position upon the vertical supporting rods. At the top of the spindle is clamped a brass boss, V, carrying a plane galvanometer mirror, W, and a fibre arm, X, about 15 cm. long. The framework of the condenser, and therefore the rotating vane, is earthed by attachment to an earthed base-plate, as, also, is a tin-plate screen which covers the effective parts of the condenser. The two semi-annular rings are connected to a stiff wire which, passing through a hole in the screen, constitutes the " live " terminal.

FIG. 4.
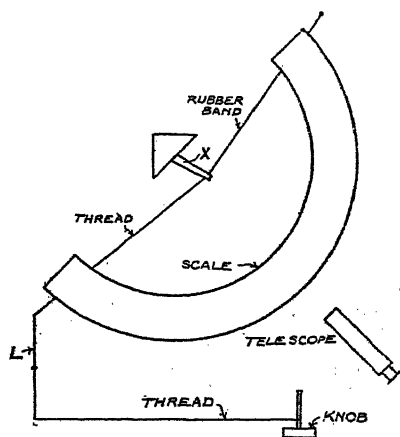
The position of the spindle is read by means of a telescope and a semi-circular scale about 150 cm. in length, as shown in Fig. 4. The mirror on the spindle is at the centre of the scale and the telescope is aligned upon it : thus a rotation of the spindle of 90° corresponds to about 1500 mm. on the scale. The reading of the scale can be made within 0·2 mm., and the adjustment of the rotation of the spindle with this degree of accuracy is accomplished quite simply in the following manner.

To the tip of the fibre arm, X, a long thread is attached which passes to one end of a wooden lever, L, 30 cm. long, pivoted at its middle point. To the other end of the lever is attached a second thread which is wound upon a thin brass rod provided with a knob and rotating stiffly in a cork that is clamped rigidly. Turning the knob thus rotates the spindle of the condenser. The threads are

kept taut and the spindle is returned in the other direction by the tension of a stout rubber band. The wooden lever is introduced into the system in order that the adjusting knob may be near the hand of the operator whilst he is at the telescope at a distance from the condenser.

The design of variable condenser here described has the following important advantages :

(1) Consistency of resetting is obtained by the use of conical bearings.

(2) Great accuracy of setting and reading is attained in the manner already described.

(3) Freedom from external capacity effects is ensured by the earthing of the moving system, adequate screening, and remote control.

(4) The calibration curve is free from the irregularities that arise in the usual vane type of condenser through the effects of the spacing washers and supports.

(5) A simple adjustment of the range of capacity within wide limits is attained by alteration of the positions of the ebonite platforms, T (Fig. 3).

The complete assembly of the apparatus is shown diagrammatically in Fig. 1. The dielectric container, C_4, and the wide-range condenser, C_3, are connected in parallel with an inductance, L_3, which, for frequencies of the order of $10^6 \sim$ per second, consists of 30 well-spaced turns of No. 16 S.W.G. copper wire wound upon a spirally-grooved ebonite tube, 9 cm. in diameter. L_1 and L_2 are " honeycomb " inductances of the type commonly used in radio-telegraphy; C_2 is a variable condenser of the ordinary vane type, having a maximum capacity of approximately $300\mu\mu F$; and C_1 is a mica-dielectric " by-pass " condenser of approximately $0\cdot01\ \mu F$. B_1 is a dry-cell battery of 50 volts and B_2 a 4 volt. 100 amp.-hour accumulator; G is a uni-pivot galvanometer having a sensitivity of about $1\mu A$. per scale division. R_1, a potentiometer of 500ω, and R_2, a resistance of 900ω, are adjusted so as to neutralise the greater part of the anode current through G (Dowling, *loc. cit.*, p. 175).

Although the construction of C_v was adapted to secure a recti-linear relationship between scale reading and capacity, it was intercalibrated throughout its range by substituting for C_4 a very small, fixed-capacity condenser the capacity of which was measured in terms of scale divisions of C_v at a large number of places along the scale of the latter. If the " scale-division : capacity " ratio had been truly rectilinear, the apparent value of the very small condenser would have been precisely the same at all points along

the scale. The apparent values obtained gave the data necessary for the preparation of a correction-curve to express all readings in terms of " mean scale divisions." Finally, the capacities of the six fixed-capacity condensers, C_a to C_f, were measured in terms of scale divisions of C_v (for $C_a \approx C_v$, $C_b \approx C_a + C_v$, $C_c \approx C_a + C_b + C_v$, and so on). The capacity corresponding to a mean scale division of C_v is thus the unit in all measurements.

Having thus intercalibrated C_3, the capacity of C_4, containing dry air at a known pressure and at the temperature of the thermostat, is measured in terms of C_3. To do this, C_4 is switched out of circuit and, with C_3 at a large setting, L_1C_2 is adjusted to approximate resonance with L_3C_3. Exact resonance between the two circuits is then obtained by varying C_v and is shown by a sharp minimum reading of the galvanometer, G, and the reading of C, is taken. C_4 is then switched into circuit and C_3 is reduced in value until resonance is again obtained between the two circuits. This reduction in C_3 is a measure of the capacity of $C_{4(air)}$. Finally, C_4 is filled with the liquid under examination (at the temperature of the thermostat), and its capacity measured as before. The latter capacity, $C_{4(liquid)}$, divided by the former, $C_{4(air)}$, gives the dielectric constant of the liquid to a standard of $\epsilon_{(air)} = 1$, at the temperature and frequency of the measurement. Shortly before or after the measurement, the frequency is determined by means of a heterodyne wave-meter (Sayce, *Expt. Wireless*, 1923, **1**, 70). The value of the dielectric constant so obtained can be corrected to a vacuum standard by making use of recent determinations of the specific inductive capacity of air (Carman and Lorance, *Physical Rev.*, 1922, **20**, 715; Gill, *Radio Rev.*, 1921, **2**, 450; Wagstaff, *Phil. Mag.*, 1924, [vi], **47**, 66).

Experimental Difficulties and Precautions.—When first applied, the method gave inconsistent results, due to slight temperature changes in the valve, in the oscillator coils and, particularly, in the variable condenser, C_3. Sudden changes in the temperature of the valve were prevented by enveloping it in cotton-wool. The influence of sunlight upon the apparatus was so marked that it was found desirable to obscure the windows of the laboratory and illuminate the apparatus by artificial light. Ultimately, the air of the room was kept at a fairly constant temperature and, as an additional precaution, the condensers C_a to C_f were intercalibrated with C_v before and after each determination.

Results.—The following results, obtained with benzene, are given, not as having any absolute significance but simply as an example of the degree of consistency so far observed in repeated measurements on the same material. This we regard as an important

criterion of the precision of the method. The benzene was rigorously purified by fractional distillation and fractional crystallisation and was finally distilled over phosphorus pentoxide, but without any attempt to attain intensive drying.

Dielectric Constant of Benzene at 25·5°. Frequency 65 × 10³ cycles per second.

ε (air = 1) ……………	2·2380	2·2392	2·2396	2·2388
		Mean 2·2389		
Diff. from mean………	−0·0009	+0·0003	+0·0007	−0·0001
		Mean difference from mean ±0·0005.·		

It is interesting to make a comparison, as to consistency, between our results and those of Turner (Z. physikal. Chem., 1900, **35**, 385), who, using the method of Nernst (ibid., 1894, **14**, 622), applied to carefully purified benzene, obtained the following data, which are commonly cited as the most accurate available. The frequency was low but unspecified, and the results were corrected to 18°.

ε ……………	2·290	2·291	2·285	2·288	2·293	2·292	2·286
			Mean 2·289.				
Diff. from							
mean ……	+0·001	+0·002	−0·004	−0·001	+0·004	+0·003	−0·003
			Mean difference from mean ±0·003.				

During our measurements no special precautions were taken to maintain room temperature constant and there is much evidence that even the small differences here recorded are due to small changes in the temperature of the various parts of the apparatus. Hence it seems probable that, under more constant temperature conditions, still greater precision may be attained by the method.

Note.—Since the completion of the above measurements, a further contribution to the measurement of dielectric constants has been made by Grützmacher (Z. Physik, 1924, **28**, 342). Results for benzene, stated to the fourth decimal place and, from internal evidence, probably significant to the third decimal place, are there given, but as only one result is recorded for each temperature we are unable to compare the consistency of the measurements with that obtained by our method.

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L.—*Studies in Electro-endosmosis. Part III.*

By FRED FAIRBROTHER and HAROLD MASTIN.

IN the first paper of this series (J., 1924, **125**, 2319), a method was described for the measurement of electro-endosmosis and at the same time of the potential gradient across the diaphragm. The

method was illustrated by measurements of the effect of acid and alkali on the electro-endosmosis through a diaphragm of carborundum powder. An account is now given of the effect of a number of other ions on the same diaphragm.

With the exception of a few experiments of Perrin, using sodium bromide and lanthanum nitrate in neutral or weak alkaline solution, there appear to be no data respecting the effect of ions other than hydrogen and hydroxyl on the electro-endosmosis through a diaphragm of carborundum powder.

A word may be said on the choice of a suitable diaphragm material for making unambiguous electro-endosmotic measurements. This is not particularly easy. It is clearly desirable that there should be no doubt as to whether the surface of the solid phase is attacked chemically by the solute or solvent. In this connexion, it is illuminating to study the conductivity of a dilute solution in some powder which *en masse* may appear quite resistant chemically, as, for example, powdered crystalline alumina. The conductivity of the mixture alters considerably with time, increasing or decreasing according to the previous history of the powder. Quartz, particularly if finely powdered, in some solutions, suffers from the same complaint in a lesser degree. Carborundum, on the other hand, possesses a surface which is very resistant to chemical action.

Experimental.

The experimental details of the measurements were as given in Part I. The potassium salts were obtained as pure as possible by recrystallisation; the aluminium chloride was Kahlbaum's "Kaufliche." The dilute solutions were made up by the progressive dilution of stronger standard ones. The aluminium chloride and thorium nitrate solutions were made from stock solutions originally of about $M/10$-strength; these were standardised after the hydroxide had settled out. The factor of the aluminium chloride was 0·86 and of the thorium nitrate 0·91, both with respect to the kation.

It is desirable, as McBain (*J. Physical Chem.*, 1924, **28**, 706) has pointed out, to give the full experimental data, in view of the assumptions made in calculating ζ. In the present case, this would require a prohibitive amount of space for the figures. On the other hand, it would be misleading to give averages of the velocities and potential gradients, since ζ is not a linear function of these magnitudes.

The following plan has therefore been adopted : in Table I, Γ refers to the volume of liquid transported in each experiment, whilst T and E refer respectively to the time and the potential gradient across the diaphragm in a single typical estimation. From

these figures ζ_T has been calculated. Under $\zeta_{av.}$ are given the average values of ζ from N different observations. The present estimations, with the exception of those in barium chloride solutions, were in general much more uniform and reproducible than those in water or acid or alkaline solutions. ζ has been calculated in each case on the basis of the calibration of the diaphragm with $N/10$-potassium chloride.

TABLE I.

Electrolyte.	Conc.	V c.c.	T secs.	E volts.	ζ_T volt.	N.	$\zeta_{av.}$ volt.
KCl	$N/50,000$	0·30	33·7	69·0	−0·0729	14	−0·0729
,,	$N/12,500$	0·20	31·6	53·6	−0·0667	14	−0·0666
,,	$N/3125$	0·15	27·3	51·5	−0·0602	13	−0·0604
,,	$N/781·2$	0·10	34·1	35·0	−0·0473	12	−0·0469
,,	$N/195·3$	0·05	35·0	26·8	−0·0301	11	−0·0302
,,	$N/48·8$	0·02	29·2	21·4	−0·0181	11	−0·0171
K₂SO₄	$N/50,000$	0·20	31·9	43·1	−0·0821	16	−0·0820
,,	$N/12,500$	0·15	33·8	34·7	−0·0722	18	−0·0722
,,	$N/3125$	0·05	33·1	15·5	−0·0550	9	−0·0542
,,	$N/781·2$	0·07	33·4	24·3	−0·0487	8	−0·0487
,,	$N/195·3$	0·04	33·1	19·5	−0·0350	10	−0·0351
K₄Fe(CN)₆	$N/50,000$	0·15	29·1	45·9	−0·0634	13	−0·0635
,,	$N/12,500$	0·10	25·3	40·7	−0·0548	16	−0·0541
,,	$N/3125$	0·10	42·8	26·4	−0·0500	14	−0·0491
,,	$N/781·2$	0·04	38·0	16·0	−0·0372	10	−0·0371
,,	$N/195·3$	0·04	32·0	19·5	−0·0362	4	−0·0338
,,	$N/48·8$	0·02	34·7	12·0	−0·0271	16	−0·0262
BaCl₂	$N/100,000$	0·10	26·1	43·8	−0·0494	12	−0·0486
,,	$N/50,000$	0·10	26·2	50·1	−0·0430	12	−0·0431
,,	$N/12,500$	0·10	31·5	43·7	−0·0410	12	−0·0410
,,	$N/3125$	0·05	30·8	33·8	−0·0271	8	−0·0282
,,	$N/781·2$	0·02	26·3	17·8	−0·0241	10	−0·0244
,,	$N/195·3$	0·03	40·6	49·1	−0·0085	7	−0·0085
,,	$N/48·8$	0·02	38·4	38·1	−0·0039	6	−0·0054
AlCl₃							
(F = 0·85)	$N/800,000$	0·20	24·5	68·8	−0·0670	14	−0·0670
,,	$N/400,000$	0·15	26·6	63·6	−0·0501	12	−0·0501
,,	$N/200,000$	0·06	31·6	77·7	−0·0138	18	−0·0137
,,	$N/100,000$	Small, but distinctly positive charge on the carborundum.					
,,	N/50,000	0·05	26·6	57·6	+0·0184	14	+0·0184
,,	$N/12,500$	0·06	26·7	31·3	+0·0406	19	+0·0402
,,	$N/3125$	0·10	32·1	41·9	+0·0420	15	+0·0422
,,	$N/781·2$	0·10	42·0	33·8	+0·0398	11	+0·0398
,,	$N/195·3$	0·05	28·4	28·3	+0·0351	12	+0·0350
Th(NO₃)₄							
(F = 0·91)	$N/800,000$	0·25	30·4	65·6	−0·0708	18	−0·0706
,,	$N/400,000$	0·15	35·0	42·8	−0·0565	9	−0·0574
,,	$N/200,000$	0·01	23·9	20·0	−0·0118	12	−0·0116
,,	$N/100,000$	0·10	22·7	70·6	+0·0352	16	+0·0352
,,	$N/50,000$	0·10	22·8	46·2	+0·0536	16	+0·0536
,,	$N/12,500$	0·15	26·1	40·6	+0·0799	11	+0·0798
,,	$N/3125$	0·15	30·6	33·7	+0·0822	12	+0·0822
,,	$N/781·2$	0·10	26·6	28·8	+0·0737	16	+0·0735
,,	$N/195·3$	0·07	26·7	23·9	+0·0619	16	+0·0618

The mean values of ζ are shown graphically on the accompanying diagram.

The values for distilled water showed greater variation than those for the solutions; — 0·0698 volt, the mean of fifteen independent determinations, has been adopted as a probable figure.

The results may be summarised as follows : Anions have comparatively little effect; the quadrivalent ferrocyanide ion appears to be slightly abnormal. Kations tend to annul, and then, in the

FIG. 1.
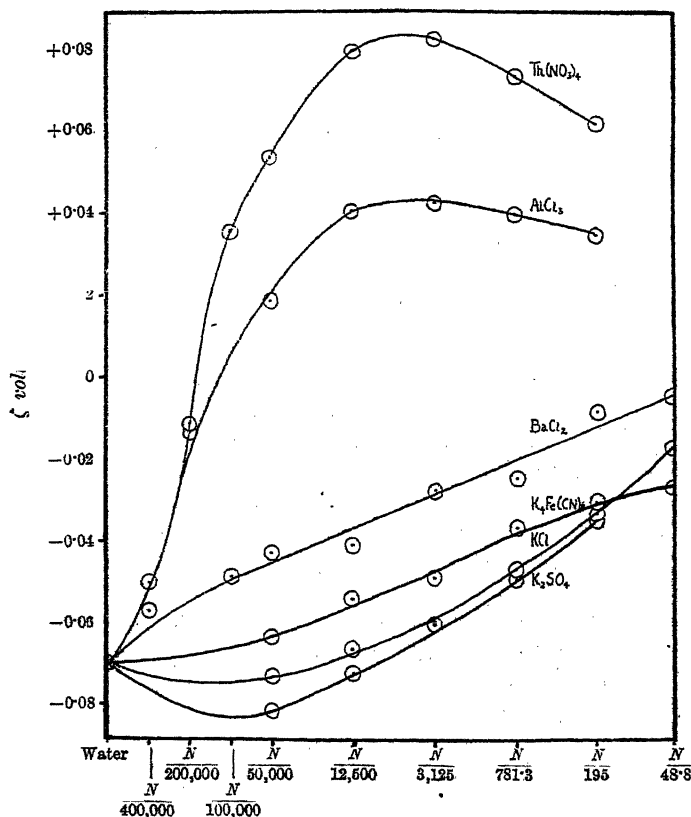
case of ter- and quadri-valent ions, to reverse the sign of the charge of carborundum in water, which is originally negative. The effect becomes much more marked as one passes from univalent potassium to bivalent barium and on to ter- and quadri-valent ions. Al··· and Th···· give a maximum positive charge to carborundum at about $N/4000$. It may be noted that Al··· and Th···· produce an appreciable effect even at a concentration of $5·0 \times 10^{-6}N$, the sign of the charge being reversed at $10^{-5}N$. At these dilutions,

the conductivity due to the added salt is of the same order as, or even less than, the conductivity of the water. $10^{-5}N$-Aluminium chloride contains only a few tenths of a milligram of salt per litre.

In very low concentrations of potassium salts, the value of ζ is higher (more negative) than in water. This may be discounted to some extent on account of experimental error due to contamination with atmospheric carbon dioxide. On the other hand, ζ in $N/50,000$-potassium sulphate was more negative than the most negative water value obtained.

There are no electro-endosmosis results with which the present ones can be directly compared, but there is a striking similarity between them and Kruyt's (*Kolloid-Z.*, 1918, **22**, 81) values for the effect of kations on stream potentials in glass capillary tubes. Kruyt found that the charge of the glass capillary tube was reversed in sign in aluminium chloride of a concentration of 1 micro-mol. per litre, which is even lower than that found for carborundum in the present work. Kruyt also obtained maximum negative values for the charge on glass in extremely dilute solutions of several salts.

A close parallel to this increase of negative charge in very dilute solution is found in some recent work of Alty (*Proc. Roy. Soc.*, 1924, **106**, 315), who found that the velocity of cataphoresis of air bubbles in water varied with the conductivity of the water. He states : " The results . . . indicate that the reduction of charge does not commence until a definite concentration of ions is reached, while below this the ions have the reverse effect and augment the bubble velocity." The foregoing results indicate that with carborundum, at any rate in solutions of potassium salts, the same is true. In solutions of salts of ter- and quadri-valent ions, the concentrations below which an increase of negative charge could take place are so very low that experimental errors due to carbon dioxide and other dissolved impurities make it very difficult to obtain trustworthy data.

Summary.

(1) The effect of anions and kations on electro-endosmosis through a diaphragm of carborundum powder has been examined. Kations tend to annul the (negative) electrokinetic potential of carborundum against aqueous electrolytes and, in the case of ter- and quadri-valent ions, to charge the carborundum positively against the solution.

Anions have comparatively little effect.

(2) $Al^{...}$ and $Th^{....}$ reverse the sign of the charge at concentrations of only a few micro-mols. per litre.

(3) In very low concentrations of potassium salts the carborundum is more negative than in water.

(4) The present results show a great similarity to Kruyt's results for stream potentials in glass capillary tubes.

LI.—*A Comparison between the Homogeneous Thermal Decomposition of Nitrous Oxide and its Heterogeneous Catalytic Decomposition on the Surface of Platinum.*

By CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD.

MUCH interest lies in the problem of the conditions under which catalytic reactions take place at solid surfaces, and for the elucidation of such heterogeneous changes one of the first necessities seems to be the careful comparison of a number of catalysed with the corresponding uncatalysed reactions. But no complete study appears hitherto to have been made of a simple change caused to proceed on the one hand in the homogeneous gaseous phase and on the other hand at the surface of a solid catalyst. The difficulty has always been to realise experimentally the conditions for isolating the two types of reaction so that they may be separately investigated. Such a comparative study is made in this paper for the thermal decomposition of nitrous oxide. The kinetics of the homogeneous reaction were described in a previous paper (*Proc. Roy. Soc.*, 1924, [*A*], **106**, 284) and experiments on the heterogeneous reaction at the surface of a platinum wire are now added. The homogeneous reaction is bimolecular, and at 795° is unaffected by the presence of platinum foil; thus if any reaction takes place at the surface of the platinum, it is slow compared with the homogeneous change and cannot be measured. If, however, a wire is heated electrically, it should be possible to find a temperature where the surface reaction attains a measurable speed, and by keeping the bulk of the gas cold the homogeneous reaction should be eliminated, since at a distance from the wire of the order of a mean free path the temperature of the gas falls several hundred degrees below that of the wire. It was realised that the homogeneous reaction proceeding in a thin layer of gas round the wire might be a serious factor, but experiments made with two different platinum wires over a range of temperature from 600—1200° showed

that the reaction under these conditions was the true surface reaction.

The Apparatus.—The essential part of the apparatus consists of a cylindrical bulb about 16 cm. long and 3·5 cm. in diameter, with the platinum wire stretched axially and sealed through small plugs of glass at the ends. Leads of negligible resistance connect with the battery of accumulators, rheostat, ammeter, and a voltmeter in parallel with the heated wire. Capillary tubes lead to a Gaede pump, nitrous oxide supply, and a capillary manometer. The reaction bulb is kept immersed in melting ice.

Determination of the Temperature of the Wire.—Simultaneous readings of ammeter and voltmeter while the wire was heated gave its resistance to within 0·2%. From this the temperature of the wire was calculated, the resistance at 0° and the temperature-resistance curve of the wire having been separately measured. A correction, which amounted to about 5%, was made for the resistance of the unheated portion of the wire passing through the seals. Since the brightness of the wire appeared uniform along the whole length, the temperature was probably quite uniform, as was to be expected from the axial situation of the wire and the absence of any bends or loops. With regard to constancy and reproducibility, the temperature was probably controllable to within a degree or two in the region of 1000°, and although this cannot be claimed for the absolute values of the temperature, owing to the end corrections, these values should be substantially correct. It may be mentioned here that the two wires with rather different temperature-resistance curves gave concordant values for the temperature coefficient of the reaction velocity. Thermal equilibrium was established within a second when the current was switched on, and remained quite steady as long as the bulb was kept in ice.

Method of Experiment.—Nitrous oxide at a known pressure was let into the apparatus at 0°. The current was switched on for a suitable period, measured by a stop-watch, and then switched off. The wire cooled instantly and the pressure of the gas was again measured at 0°. The increase gave the amount of decomposition. The current was then switched on again and the process repeated. As the reaction proceeded, the thermal conductivity of the gas changed slightly, and rather more energy had to be supplied to keep the temperature constant. With nitrous oxide at a pressure of 200 mm., an initial voltage of 10·00 would need to be raised to 10·20 during the reaction to keep the resistance of the wire at its original value.

Figs. 1 and 2 show that quite regular curves are obtained by plotting decomposition against time. When the wire was in good

condition, very concordant results could be obtained, as the following figures show :

Time (secs.)	300	600	900
%.....................	37⎱ 36⎰	52⎱ 52⎰	62⎱ 61⎰

The Influence of Pressure.—The influence of pressure is remarkable, the percentage decomposition in a given time increasing as the initial pressure of nitrous oxide diminishes, in striking contrast with the homogeneous reaction. The curves in Fig. 1, obtained with wire 2 at 909°, illustrate this.

There is no question of the results being affected by a drift in the activity of the platinum, since a final experiment at 200 mm.

FIG. 1.
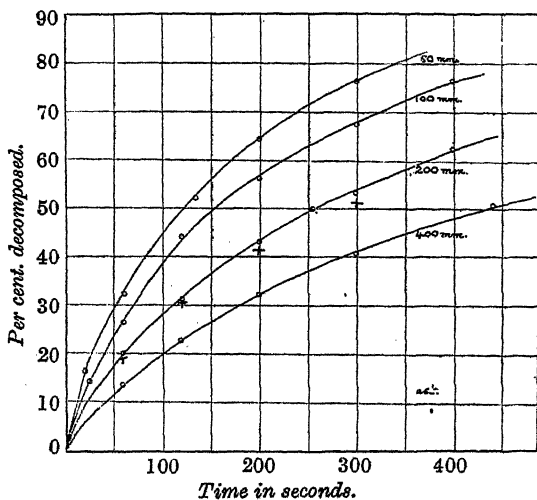
Influence of initial pressure on catalytic decomposition of nitrous oxide.

The points marked with circles on the 200 mm.-curve were obtained in the first experiment of the whole series ; those marked with crosses, in the last.

agreed well with the first. The times required for half the nitrous oxide to decompose, " half-life," were as follows :

Initial pressure of N_2O in mm.	50	100	200	400
Half-life in seconds	110	145	242	395

Another set of experiments with wire 1 at 889° gave

Initial pressure	100	200	400
Half-life in seconds	540, 590	1290, 1230	3690

The explanation is as follows. It is shown in the next section that the oxygen formed in the decomposition retards the reaction. The retardation depends upon the fraction of the platinum surface

covered by adsorbed oxygen and this in turn depends upon the absolute pressure of the oxygen, not upon its pressure relative to that of the nitrous oxide. Hence the retardation by oxygen is through every stage of the reaction greater for high than for low initial pressures of nitrous oxide.

The Influence of Added Oxygen and of Nitrogen.—Nitrogen appeared to have a slight retarding influence, but almost negligible in comparison with that of oxygen. These influences are shown by the following table and by the curves in Fig. 2 :

	Per cent. decomposed in			
	100	200	300	400 secs.
200 mm. N_2O	28	43	53·5	60
200 mm. N_2O + 100 mm. N_2	22·5	38·5	48·5	55
200 mm. N_2O + 200 mm. N_2	19·5	34	43	51
200 mm. N_2O + 100 mm. O_2	2	4	6	10

FIG. 2.
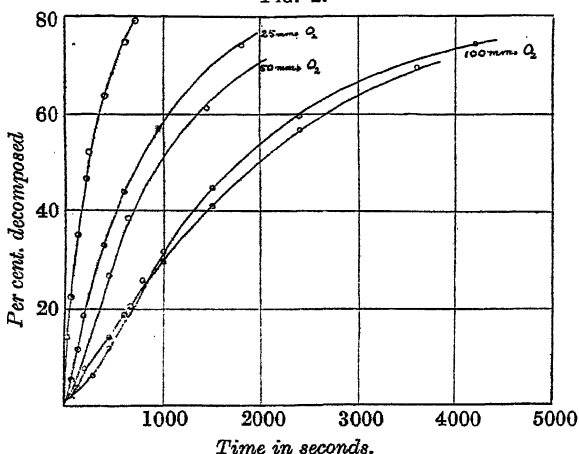
Influence of oxygen on the catalytic decomposition of nitrous oxide. Initial pressure of N_2O = 200 mm. Temperature 910°.

The quantitative relation between oxygen pressure and initial velocity was now examined. Nitrous oxide and oxygen at known pressures were introduced and the wire was heated for 60 seconds. The percentage decomposition in this time gave an approximate measure of the reaction velocity. Between the experiments the wire was heated to a standard higher temperature (1500°) in a vacuum to drive out any oxygen which had started to dissolve in the wire.

Pressure of N_2O, 200 mm. in each case. Temperature 911°. p = average pressure (mm.) of oxygen. r = observed rate of reaction as percentage in 60 seconds. s = rate calculated from the expression $64/(1 + 0·02 p)$.

p	23	40	74·5	112	159	206	257	305
r	46	35	29	20	14	10	10	10
s	44	36	26	20	15	12·5	10·4	9

Thus the oxygen adsorption seems to follow an isotherm of the type discussed in Freundlich's " Kapillarchemie," 2nd edition, 1922, p. 175 *et seq.*

If σ be the fraction of the surface covered by the retarding film and $1 - \sigma$ the fraction free, then for equilibrium, equating the rate of condensation and the rate of evaporation at a given oxygen pressure, p, we have $c_1\sigma = c_2(1-\sigma)p$, c_1 and c_2 being constants, whence $1 - \sigma = c_1/(c_1 + c_2 p) = 1/(1 + bp)$, where $b = c_2/c_1$. Thus the rate of reaction should be proportional to $1/(1 + bp)$. The bottom line of the above table shows that this is adequately fulfilled.

The Dynamics of the Reaction.—All the observed phenomena are adequately expressed by the equation

$$- \frac{d[N_2O]}{dt} = \frac{k[N_2O]}{1 + b[O_2]} \quad \text{or} \quad \frac{dx}{dt} = \frac{k(a - x)}{1 + bx}$$

whence
$$k = \frac{1 + ab}{t} \log_e \frac{a}{a - x} - \frac{bx}{t}.$$

The equation may be tested by the following criteria :

1. For a given pressure of oxygen the initial rate of reaction is proportional to the pressure of nitrous oxide, or, expressed as a *percentage*, is independent of the pressure. Thus, with 100 mm. O_2 added initially, the following initial rates were found : 100 mm. N_2O, $1\cdot0\%$ per minute; 30 mm. N_2O, $1\cdot0\%$ per minute; 100 mm. N_2O, $1\cdot0\%$ per minute.

2. The retarding influence of added oxygen is satisfactorily expressed.

3. It expresses the decrease in the " half-life " of the nitrous oxide with diminishing pressure. Thus the " half-life," τ, is given by $1/k\{(1 + ab) \log_e 2 - ab/2\}$; if we take the half-life at 200 mm. as unity, and b as $0\cdot020$, the values are :

Initial pressure	100 mm.	200 mm.	400 mm.
τ (calc.)	0·74	1·00	1·53

A set of ratios found for a wire having a b value of approximately $0\cdot020$ were actually $0\cdot60$, $1\cdot00$, $1\cdot63$.

4. Its quantitative accuracy may be tested as follows. If in the integrated equation we put $1/t \log_e a/(a - x) = k_m$ and $x/t = v$, it will be seen that k_m should be a linear function of v, and the linearity of the relation is a characteristic test of the form of the equation, not influenced by the choice of the constants, which only determine the slope of the line and its intercepts on the axes. Since $v = (a + 1/b)k_m - k/b$, the slope will be $a + 1/b$ and the intercept on the v axis will be $- k/b$, whence k and b may be found. The following two experiments are quoted as typical of many.

Temperature 911°. $a = 95$.

	t (secs.).	$v = x/t$.	$k_m =$ $1/t \log a/(a-x)$.	$v + 0.190$.	$\dfrac{v + 0.190}{k_m}$ $a + 1/b$.
10	20	0·500	0·00558	0·690	123·8
20	50	0·400	0·00473	0·590	124·6
30	90	0·333	0·00422	0·523	124·1
40	150	0·266	0·00364	0·456	125·7
50	225	0·222	0·00332	0·412	124·0
60	337	0·178	0·00296	0·368	124·3
70	500	0·140	0·00267	0·330	123·8
80	740	0·108	0·00249	0·298	119·8
					Av. 124·3

The linear relationship is shown by Fig. 3 and by the last column. The intercept on the line $k_m = 0$ is -0.190. Thus $k/b = 0.190$ and since $a + 1/b = 124.3$, we have $k = 0.00647$ and $b = 0.0341$.

Temperature 741°. $a = 95$.

	t (secs.).		k_m.	$v + 0.0135$.	$(v + 0.0135)/k_m$
10	315	0·0318	0·000353	0·0453	129·3
20	750	0·0267	0·000315	0·0402	127·8
30	1400	0·0214	0·000271	0·0349	128·6
40	2250	0·0178	0·000243	0·0313	128·8
50	3450	0·0145	0·000216	0·0280	129·5
60	5150	0·0116	0·000194	0·0251	128·9

whence $k = 0.000400$ and $b = 0.0296$.

FIG. 3.
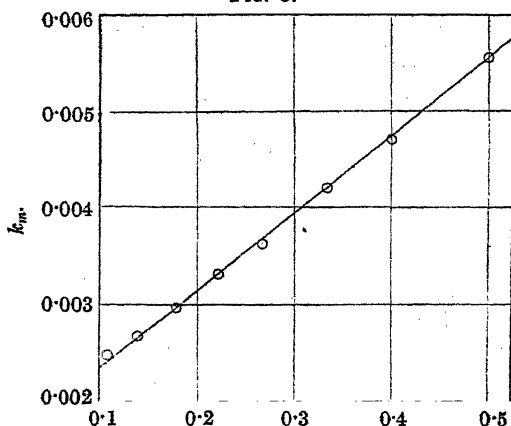
It will be seen that whereas k varies in these two experiments 16-fold between 741° and 911°, the variation in b is very much smaller. Thus the retarding effect of the oxygen does not vary very markedly with temperature.

The Influence of Temperature.—Two series of experiments were made with different wires.

First wire. Fig. 4 shows the effect of temperature on the initial

velocity as measured by the reciprocal of the time required for the decomposition to reach 10% (initial pressure 200 mm.)—this initial velocity being used so that any influence of the oxygen retardation would be reduced to a minimum. The value of the heat of activation obtained from the slope of the curve is 35,000 calories per gram-molecule, and is seen to be constant within the limit of experimental error.

t = Time (secs.) for decomposition to reach 10%.

$T°$ (abs.)	t.	$\log_{10} t$.	$1/T \times 10^7$.	$T°$ (abs.)	t.	$\log_{10} t$.	$1/T \times 10^7$.
1506	13	1·11	6642	1109	470	2·67	9,023
1448	9	0·95	6906	1085	500	2·70	9,214
1394	25	1·40	7172	994	4,300	3·63	10,060
1324	38	1·58	7554	944	9,300	3·97	10,590
1204	140	2·15	8307	893	29,000	4·46	11,200

FIG. 4.
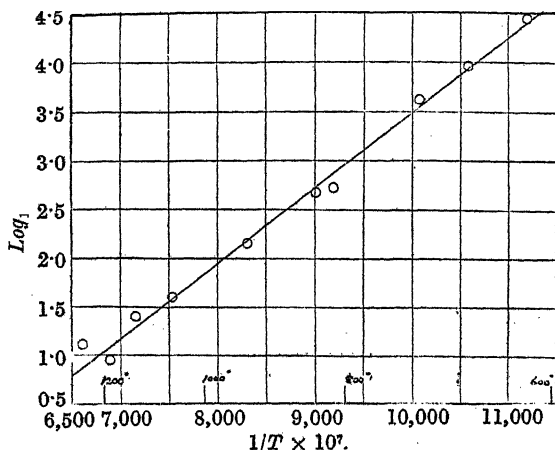
Influence of temperature on the heterogeneous decomposition of nitrous oxide on a platinum wire.

Second wire. The surface area of this wire was 1·5 times as great as that of the first. At corresponding temperatures it was about 3 times as active. The following is a brief summary of the results. The initial pressure of nitrous oxide was 200 mm.

Time in seconds for decomposition to go from

$T°$ (abs.).	0— 10%.	10— 30%.	30— 50%.	$T°$ (abs.).	0— 10%.	10— 30%.	30— 50%.
1323	12·5	27	37	1180	26	77	147
1275	18	35	49	1130	90	290	550
1228	19	48	88	1065	116	534	1,400
1184	20	70	135	1014	315	1085	2,050
1181	32	88	180	954	1230	6570	25,200

The heats of activation were obtained separately for the ranges 0—10%, 10—30%, 30—50%, from the graphs of $1/T$ and log t. The values were 33,000, 36,800, and 42,500. Whence, by extrapolation to zero decomposition, the value 31,500 is found. Applying an equal correction to the previous value of 35,000, we have for the heat of activation corresponding to initial velocities

First wire   33,500 calories $\Big\}$ Mean *32,500 calories.*
Second wire 31,500 calories

Behaviour of the Platinum. Final Proof that the Reaction is Heterogeneous.—The activity of the annealed platinum wires was satisfactorily reproducible unless they had been in contact with oxygen at fairly high pressure. This treatment tended to cause a gradual and progressive diminution in activity from one experiment to another, indicating an actual solution of the oxygen in the platinum distinct from the reversible surface adsorption. The following experiments, carried out at the end when there was no longer any need to keep the wire in a constant condition, bring the effect clearly to light. The wire, which in its normal condition had caused the decomposition of 46% in 200 seconds at 910° and 200 mm. N_2O, was heated at about 1400° in an atmosphere of oxygen and allowed to cool in the oxygen, which was then pumped off. It now caused the decomposition of 3% only, under the same conditions as before. After heating in a vacuum once more to a high temperature, it regained more than its original activity, decomposing 56·5% in 200 seconds.

It is important to note that, since poisoning the wire by dissolved oxygen can cut down the rate of change from 46% in 200 seconds to 3%, the heterogeneous nature of the reaction is conclusively shown.

Comparison of the Heterogeneous Decomposition of Nitrous Oxide with its Homogeneous Decomposition.—The homogeneous reaction depends upon the collision of two molecules whose energy together exceeds 58,500 calories (in terms of *gram*-molecules). The catalytic decomposition, on the other hand, is a unimolecular process. The unimolecular change $N_2O = N_2 + O$ could not occur homogeneously at 1000° at more than a negligibly small rate compared with the other reactions, since it would involve the production of atomic oxygen and the absorption of about 60,000 calories. The heat of activation would therefore probably be enormous. In the catalytic reaction the function of the surface is thus to act as an acceptor for atomic oxygen, thereby rendering possible a unimolecular in place of a bimolecular process. This must be regarded as the principal function of the catalyst.

What makes the odd oxygen atom more easily detachable is its

affinity either for the platinum or for atomic oxygen already on the platinum. Three mechanisms are conceivable : 1. Nitrous oxide gives its oxygen atom to the bare platinum surface. A retarding film of atomic oxygen forms. 2a. Nitrous oxide reacts by striking atomic oxygen already on the platinum. 2b. Nitrous oxide reacts with atomic oxygen in gaps in a film of the latter (mechanism analogous to that suggested for interaction of nitrous oxide and hydrogen on platinum). (1) is the natural and probably correct explanation, leading to the correct equation for the reaction velocity. The one difficulty which it presents arises from Langmuir's statement (*Trans. Faraday Soc.*, 1922, **17**, 653) that even at 1500° Abs. and very low pressures platinum remains completely covered with atomic oxygen. If this is true, the retarding film which forms during the decomposition of nitrous oxide, and which is only half completed at about 60 mm. O_2, would have to be of a new kind, namely, a layer of molecular oxygen adsorbed on the primary layer of atomic oxygen. Mechanism (2a), otherwise inadmissible, would then have to be assumed. But Langmuir's statement may not be true of the platinum wires used by us, and then there is no need to go beyond (1). (It will not do to assume that the presence of nitrous oxide interferes with the completion of the oxygen film, since this would imply fairly strong adsorption of the nitrous oxide itself, in which case the velocity equation would not be of the right form.) (2b) could apply only if the atomic oxygen film covered nearly the whole surface from quite small pressures, because otherwise the greatest velocity would not be at the beginning of the reaction when there is little or no oxygen present. Nitrous oxide reacting in gaps in a nearly complete film would obey the equation—$d[N_2O]/dt = k[N_2O]/[O_2]$. This demands inverse proportionality of rate to oxygen pressure, to which simple form the actual relation does not reduce. The balance of evidence is in favour of (1) and an oxygen film half complete at 60 mm.

With regard to the various energy relationships :

Homogeneous reaction, E = 58,500 calories for 2 gram-molecules.
Surface reaction, E = 32,500 calories for 1 gram-molecule.

Although the real physical significance of E is abundantly shown for homogeneous reactions, in surface reactions it is a more complex quantity. If the attempted extrapolation of E to zero decomposition really eliminates the influence of the oxygen film, then it is probable that 30,000 calories is of the right order for the actual energy of activation. It would then appear that the catalytic reaction has a great advantage over the hypothetical homogeneous unimolecular reaction, which would demand a minimum activation of 60,000 calories per gram-molecule.

The average activation required by a single molecule in the bimolecular homogeneous reaction is 29,250 calories, so that, molecule for molecule, the catalytic reaction appears to have little advantage from the point of view of energy; we may therefore conclude that the main function of the catalyst in this case is to render possible a unimolecular process in place of one requiring the co-operation of two simultaneously activated molecules.

It may perhaps be pointed out in conclusion that any attempt to place a "quantum" interpretation upon the fact that the experimentally determined E for the catalytic reaction is about half that for the homogeneous reaction is to be deprecated. Such attempts are not in the least justified.

Summary.

The heterogeneous thermal decomposition of nitrous oxide on a platinum wire has been investigated between 600° and 1200°, the homogeneous change at these temperatures being eliminated by heating the wire only.

The reaction is retarded by oxygen, and proceeds relatively faster at low than at high pressures.

The velocity is represented by the equation :

$$- d[N_2O]/dt = k[N_2O]/(1 + b[O_2]).$$

The experimentally determined heat of activation in the catalytic reaction is 32,500 calories per gram-molecule.

A comparison is made of this catalytic reaction with the homogeneous bimolecular decomposition, and with the hypothetical homogeneous unimolecular decomposition, and the mechanism of the catalysis discussed.

LII.—*The Hydrolytic Decomposition of Phosphorus Trichloride.*

By ALEC DUNCAN MITCHELL.

THE reactions of phosphorous and hypophosphorous acids, which have been studied by the author during the last 4 years, have led to the conclusion that each of these acids exists in two forms, of which one is relatively inert (especially in the case of hypophos-

phorous acid) and the other is mainly responsible for the reducing properties. Certain considerations have been advanced which point to tautomeric structures in each case, thus :

$$HPO(OH)_2 \rightleftharpoons (HO)_3P \text{ and } H_2PO(OH) \rightleftharpoons HP(OH)_2.$$
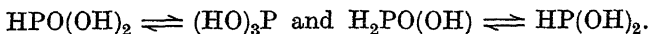
Kinetic studies of the reactions indicate that the more strongly reducing isomeride is normally present in only very small proportions, and comparison with the properties of organic analogues has been shown to suggest a tervalent phosphorus structure for this isomeride, whereas the more stable, normal form of each acid contains a quinquevalent phosphorus atom. (The term "quinquevalent" is here applied, for convenience, in the classical sense and without prejudice to the more probable co-ordinated structure.)

Such an hypothesis receives further support from a consideration of the properties of nitriles and *iso*nitriles, in which, again, the more pronounced reducing properties are associated with the lower valency of the carbon atom, and the greater stability with the higher valency.

If these views be correct, it would be expected that, during the decomposition of phosphorus trichloride by water, the compound $P(OH)_3$ would be formed as an intermediate stage which would change rapidly, but not instantly, into the ordinary form of phosphorous acid. Such a change would not be expected to be instantaneous, because the reverse change in the equilibrium has been found to be measurable.

The object of the present research was to test the truth of this deduction, and it may be stated at once that, although there are certain complications, there is considerable evidence in favour of its validity and therefore of the fundamental hypothesis.

<center>EXPERIMENTAL.</center>

The phosphorus trichloride used was the pure article of commerce and was carefully redistilled shortly before use. Its purity was checked by decomposing it with water, and, after several hours, carrying out (a) a volumetric estimation of chloride, and (b) a titration of the acidity produced, using both methyl-orange and phenolphthalein as indicators, the corresponding titres being very closely in the ratio 4 : 5 as required; the results showed the purity to be 99·6 and 99·8% as calculated from (a) and (b) respectively.

The method at first adopted was as follows. Equal weights of phosphorus trichloride (usually 1 or 2 c.c. = 1·60 or 3·20 g.) were sealed up in thin glass bulbs; one was broken by vigorous shaking in a measured volume of water at a temperature (found by control experiments) such that the heat of reaction raised the

whole mixture to 25°; after 15 seconds of such shaking, the solution appeared homogeneous and was at once mixed with a known volume of standardised iodine solution.   Definite portions were withdrawn by a pipette from time to time and titrated by standard sodium thiosulphate solution.   Other bulbs were similarly broken and the resulting solutions kept for definite periods before being allowed to react with iodine under exactly the same conditions.   The first solution effected reduction very much more rapidly than one which had been kept for, say, 30 minutes, and the latter, in turn, was considerably more reactive than one which had been kept for, say, 4 hours.   By constructing curves showing the relation between velocity of reaction and concentration of unchanged iodine, it was found that the velocity did not fall to the normal value until after the expiration of at least 2 hours, where the normal value is that given, for the same concentration of iodine, by a solution which has stood for 24 hours or by an artificial mixture of the appropriate amounts of phosphorous and hydrochloric acids.   Table I shows the results of a typical experiment in which 3·20 g. of phosphorus trichloride and 200 c.c. of water (giving 201·2 c.c. of solution) react with 10 c.c. of approximately $N/2$ iodine, the reaction being started (i) 15 seconds and (ii) 24 hours after breaking the bulbs.   Titres are shown, after intervals of time in minutes, for 10 c.c. against $N/100$-sodium thiosulphate.

TABLE I.

| | (i.) | | | (ii.) | |
Time.	Titre.	Difference.	Time.	Titre.	Difference.
0	23·59	—	0	23·59	—
1	21·03	2·56	54	20·74	2·85
6	18·59	5·00	116	19·16	4·43
9·5	17·42	6·17	171	17·87	5·72
16	16·25	7·34	223	16·73	6·86
22	15·65	7·94	275	15·67	7·92
30	15·20	8·39	351	14·17	9·42
62	14·30	9·29	405	13·20	10·39
115	13·30	10·29	480	11·87	11·72
190	11·98	11·61	536	11·00	12·59
245	11·17	12·42			
321	10·07	13·52			
371	9·33	14·26			

The initial velocity of (i) is about 60 times that of (ii), but they become equal, within the limits of experimental error, for equal concentrations of iodine, at a stage corresponding to about 115 minutes after the initial decomposition in (i).   In another experiment, using double the concentrations of phosphorus trichloride, the control was broken 3 days before starting reaction with iodine, and the other tube 31 minutes before.   The curves connecting velocity of reaction with concentration of iodine differed widely at

first, but became sensibly identical at an iodine concentration corresponding to 150 minutes of the second reaction—or 181 minutes after the initial decomposition.

It was thus obvious that the "nascent" solution contained one or more constituents, other than normal phosphorous acid, which reacted very readily with iodine and were lacking in a solution which had been similarly made and kept for 24 hours.

In order to follow the decomposition from another point of view, and also to see whether these differences were caused by the transient existence of an oxychloride, solutions were made as before, and, after 15 seconds, rapidly titrated by $2N$-sodium hydroxide.* The end-point thus reached was not permanent and the subsequent further development of acidity was followed by $N/5$-alkali. In other experiments, measured portions of the solution were withdrawn from time to time and titrated with alkali. Both methods showed that only about 98% of the final acidity was attained within 1 minute, and that the remainder was developed with decreasing rapidity during the next 30 minutes, after which no further increase could be detected. This type of experiment is exemplified in Table II, which is placed later in another connexion. The hypothetical $(HO)_3P$ would probably resemble phosphoric acid in its basicity, and, in any case, it would not behave in such a way that its change to $HPO(OH)_2$ would result in an increase of acidity; its existence would therefore not account for these observations.

The results just described made it clear that a compound of the type $P(OH)_2Cl$ persists for some 30 minutes under the conditions of experiment, and this might be responsible for a part, at least, of the enhanced reducing power. It was therefore necessary to make some more precise measurements on the persistence of this increased reducing power in order to ascertain definitely whether it outlasted the increase of acidity, or, in other words, whether it actually persisted for a period of some hours or whether it became inappreciable after 30 minutes. A more crucial type of experiment was devised : 3·2 g. (2 c.c.) of phosphorus trichloride and 200 c.c. of water at 18·4° were shaken for 15 seconds and attained the temperature of 25°; at short intervals, 20 c.c. of this mixture were mixed with 1 c.c. of $N/2$-iodine and kept for 1 minute; the mixture was then rapidly diluted and titrated with $N/50$-sodium thiosulphate. The deficiencies in titre, corresponding to iodine reduced, in the

* The titres recorded refer to phenolphthalein as indicator, but parallel results were obtained with methyl-orange, so that the use of the more alkaline end-point does not appear to have hastened the decomposition of the intermediate oxychloride. Such a possibility is also excluded by the fact that similar results were obtained by decomposing with excess of alkali.

portions used after 1,* 2, 5·5, 11, and 17 minutes were 2·56, 1·64, 1·29, 1·19, and 1·16 c.c., respectively, and the deficiency then decreased very slowly, being still perceptible after 4 hours : after 24 hours, it was 0·15 c.c., of which 0·08 c.c is due to the ordinary reaction in the 1 minute involved.

Experiments of this type showed definitely that the abnormally high reducing power outlasted the increase of acidity. Moreover, numerous experiments showed that, in the 20 minutes following the initial alkali titration, at least 89% (and usually about 93%) of the additional alkali had been added, whereas, in the same period, the reactivity towards iodine had decreased by 57% at most (and usually by only 45—50%); the hypothetical oxychloride does not, therefore, account for the whole of the observed exaltation in reducing power.

Table II illustrates two parallel experiments in each of which approximately 2 c.c. of phosphorus trichloride were decomposed by 100 c.c. of water; after definite intervals (of t minutes), 10 c.c. of the resulting solutions were (i) titrated with $2N/5$-sodium hydroxide, (ii) allowed to react for 1 minute with 1 c.c. of $N/2$-iodine. The table shows for (i) the alkali titre, and for (ii) the iodine consumption in c.c. as measured by $N/50$-sodium thiosulphate; in the case of (i) the titrated liquid was allowed to stand for a further period of t' minutes (*at the ordinary temperature*), and the titration again completed (giving the values shown as final titres), the end-points thus obtained being definite for 24 hours.

TABLE II.

	(i.)			(ii.)	
$t.$	Titre.	$t'.$	Final titre.	$t.$	Iodine consumed.
1	27·58	24	28·15	0·67	2·75
3	27·80	25	28·20	2·8	2·25
5	28·01	34	28·24	7	1·87
9	28·13	100	28·25	10	1·69
13	28·15	100	28·22	14	1·38
18	28·23	90	28·27	23	1·18
34	28·30	80	28·30	50	0·90
1320	28·29	—	—	82	0·64
				218	0·43
				1440	0·12
				Normal reaction.	0·12

Numerous experiments have all given similar results, and the curves plotted from the decrease of iodine consumption with time differ in type from those representing increase of acidity with time and indicate, in agreement with the data quoted above, that

* On a separate experiment.

a pronounced and much more persistent reducing effect is superimposed upon any similar effect which might be attributed to an oxychloride. The smallness of the titration differences and of the earlier time-intervals makes it impossible to attempt a mathematical analysis of the superimposed reducing effects, but it is possible to state that the development of acidity proceeds roughly according to a unimolecular law.

The hydrolysis was always accompanied by a very slight but definite smell of " phosphine," although its formation did not become pronounced except at much higher temperatures. It was believed that the analytical figures quoted, which were obtained after similar decomposition, together with the use of control experiments throughout, precluded the possibility that any of the excess reduction might be due to this trace of by-product, but in order to test this possibility still further, a few experiments were carried out with freshly prepared solutions made from phosphonium iodide which was intentionally not purified. About 0·2 g. was dissolved in 100 c.c. of water, thus giving a concentration considerably greater than any possible concentration of phosphine in the foregoing experiments. Within a few seconds the solution was tested with regard to (i) its acidity and (ii) its effect on iodine solution. In the former case the slight acidity remained constant for several days, and, in the latter case, the small iodine consumption was *instantaneous* and showed no decrease when tested at intervals of several hours. In neither respect, therefore, is there any evidence that the results recorded are in any way due to the accidental presence of traces of impurities of this type.

The reduction of mercuric chloride, instead of iodine, gives results similar to those described herein, but these were not investigated in detail.

It may be mentioned that the oxychloride POCl is described in the literature, and that the corresponding arsenic compound is known to react with minimal quantities of water to give $As(OH)_2Cl$, but the phosphorus analogue is not recorded.

Summary.

1. The solution obtained by the hydrolytic decomposition of phosphorus trichloride has abnormally pronounced reducing properties when first formed; after some hours, under the conditions of experiment, they become normal.

2. The solution increases in acidity for about ½-hour, although about 98% of the final acidity is developed almost instantly; the intermediate formation of an oxychloride, such as $P(OH)_2Cl$, would account for this observation.

3. The duration of increased reducing power is far longer than can be attributed to the intermediate oxychloride, and it is suggested that it may be due to the second form of phosphorous acid, $P(OH)_3$, which does not *immediately* change to the ordinary form, $HPO(OH)_2$.

4. The existence of such a second form has already been postulated by the author on other grounds.

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LIII.—*The Heats of Solution and of Decomposition of Chlorine Dioxide.*

By HENRY BOOTH and EDMUND JOHN BOWEN.

THE heats of solution and of decomposition of chlorine dioxide are not recorded in the literature. On account of the increasing connexions recognised at the present day between structural theories and thermochemical data, it was thought that these measurements would be valuable. As a convenient source of chlorine dioxide free from chlorine, the method of preparation due to Bray (*Z. physikal. Chem.*, 1906, **54**, 463) was used, giving a gas containing about an equal volume of carbon dioxide, which did not interfere with the measurements to be described. Analyses were also carried out by the method devised by Bray, which was found to give accurate results.

Heat of Solution.—A dried mixture of chlorine dioxide and carbon dioxide was passed into about 200 c.c. of water contained in a vacuum-jacketed calorimeter, the neck of which was closed by a stopper carrying leading-in and exit tubes, a Beckmann thermometer, the electrical calibrating coil, and a syphon for emptying. After the passage of a suitable quantity of gas, the rise of temperature was noted, and the liquid run out and analysed. Stirring was performed effectively by the gas current and by gentle shaking from time to time. The carbon dioxide and chlorine dioxide passing through were estimated; the heat loss owing to their specific heats was negligible, but a correction was applied for the latent heat of the water vapour carried away in the gas stream, deduced from separate experiments with air. The temperature rises were reproduced by expending electrical energy in a fine nichrome coil sealed in a very thin elongated glass bulb, using an accurate voltmeter and ammeter which had been used for other calorimetric work.

The mean of a large number of determinations was 6600 ± 200 calories per mol., independent of the concentration of the solution

produced. It is interesting to compare this with the heat of solution of chlorine monoxide, 9400 calories (Thomsen).

Heat of Decomposition.—A vacuum-jacketed, narrow-necked vessel was fitted with a cemented-in stopper carrying a leading-in tube and a small spark-gap. A thin-walled glass capillary tube reached to the centre of the vessel and contained a thermo-junction composed of 40 gauge copper and constantan wire. This was connected to a sensitive voltmeter. The vessel, previously evacuated, was filled to a pressure less than atmospheric with a dried chlorine dioxide–carbon dioxide mixture, and the gas fired with a small spark. The explosions were never violent under these conditions. A typical graph of the voltmeter readings is shown in Fig. 1. After

FIG. 1.

Time in minutes.
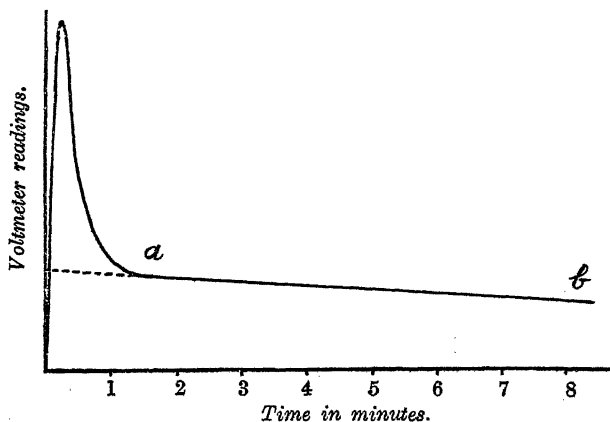
an initial large rise of temperature, the gas quickly came into equilibrium with the walls of the vessel, which had a heat capacity large compared with that of the gas. Over a long period (a—b), the rate of cooling of the walls assumed a constant small value, permitting an easy extrapolation to the time of the explosion.

For calibration, a loop of fine nichrome wire was introduced, the calorimeter being filled with air, and a suitable amount of electrical energy expended in it during a period of about 10 seconds, controlled by an accurate stop-watch. The wattage was measured with a voltmeter and ammeter which had been used before for calorimetric work. Curves of exactly the same character as Fig. 1 were obtained. A correction of 7% was found to be necessary because of the heat conducted away along the leads of the calibrating coil. The heat capacity of the coil introduced a negligible correction.

In 18 preliminary measurements the amount of chlorine dioxide

in the calorimeter during each experiment was determined by measuring the pressure, using a capillary mercury manometer, the percentage of chlorine dioxide in the gaseous mixture being determined by separate analyses. The mean value of these results was 23,500 calories per mol.

In the final experiments an evacuated vessel of known volume was connected in parallel with the calorimeter during the filling so that the same gaseous mixture entered both vessels. After disconnexion, potassium iodide solution was allowed to enter and the liquid titrated.

Other experiments showed that no undecomposed chlorine dioxide remained in the calorimeter after the explosion.

Results.—Calories per division of millivoltmeter 1·110. Titrating flask—volume 275·0 c.c. Calorimeter—volume 480·0 c.c.

No.	Neutral iodine titre (c.c.) of flask. $N/20$.	Mols. ClO_2 $\times 10^3$ in calorimeter.	Extrapolated thermo- couple divisions.	Calories.	Heat of decom- position per mol.
1	15·25	1·33	26·5	29·4	22,100
2	25·00	2·18	47·5	52·7	24,100
3	15·45	1·35	26·0	28·7	21,400
4	15·25	1·33	27·0	30·0	22,500
5	31·55	2·75	60·0	66·6	24,200

Weighted mean of all results, 23,500 calories per mol.

Taking the heat of decomposition of chlorine dioxide as 23,500 cals. per mol. from these experiments, and combining it with the heat of dissociation of chlorine, 55,000 cals. (Henglein, *Z. anorg. Chem.*, 1922, **123**, 137; Wohl, *Z. Elektrochem.*, 1924, **30**, 36), we calculate for the imaginary process of the dissociation of a chlorine dioxide molecule into a chlorine atom and an oxygen molecule

$$ClO_2 + 4000 \text{ cals.} = Cl + O_2.$$

This small difference of energy between a molecule and the free atoms composing it is important in connexion with the meaning to be attached to a "chemically active" molecule. The absorption spectrum of gaseous chlorine dioxide (Kabitz, *Diss.*, Bonn, 1905) consists of groups of lines with an approximate constant frequency difference. This grouping is well emphasised in the bands of the substance dissolved in carbon tetrachloride (Bowen, J., 1923, **123**, 1199), which have almost exactly the same positions. According to the modern theory of band spectra, these bands are to be attributed to changes of vibrational quanta superimposed upon an electronic activation quantum change. Calculating from the observed constant frequency difference of 2×10^{13} by the relation $Q = Nh\nu$, we obtain for one vibrational quantum $Q = 2000$ calories.

This deduction neglects the difference between the vibrational quanta of normal and electronically activated molecules, but this difference is neglible here. We know from the application of the quantum theory to the specific heats of gases that vibrational quanta begin to make their appearance among the molecules at temperatures not far above the ordinary temperature. Since only two vibrational quanta are necessary to give a chlorine dioxide molecule an energy equal to its dissociation products, and since, as shown in a later paper, the gas is remarkably stable thermally, it would appear that energy of vibration is not sufficient to activate a molecule chemically, but that electronic activation is required.

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OXFORD.   [*Received, December* 11*th*, 1924.]

LIV.—Cryoscopic Measurements with Nitrobenzene. Part III. Equilibrium in Nitrobenzene Solution.

By FREDERICK STANLEY BROWN.

So far as the author is aware, no example of chemical equilibrium in solution which obeys the law of mass action has been studied by the freezing-point method : most work in this direction has been done on strong electrolytes, which do not obey this law, and on associated substances, where this is doubtful. While working on associated substances, it was considered advisable to test the experimental methods by the study of examples which undoubtedly do obey the law of mass action : polynitro-aromatic compounds form, with aromatic hydrocarbons, molecular compounds which dissociate in solution in accordance with the law of mass action, as has been shown by solubility measurements (Behrend, *Z. physikal. Chem.*, 1894, **15**, 183; Kuriloff, *ibid.*, 1897, **24**, 697).

In this paper, the dissociation of naphthalene picrate and of naphthalene–trinitrotoluene in nitrobenzene solution is investigated. Previous work (Brown and Bury, J., 1924, **125**, 2219) has shown that naphthalene is a normal solute in nitrobenzene, and preliminary experiments have established the fact that trinitrotoluene and, somewhat surprisingly, picric acid are also normal.

EXPERIMENTAL.

The experimental methods have been fully described in previous papers (Roberts and Bury, J., 1923, **123**, 2037; Brown and Bury, *loc. cit.*). All work described in this paper has been carried out in moist nitrobenzene in contact with the salt hydrate pair

N*

$Na_2SO_4,0—10H_2O$. It has been found advantageous to insert a thin copper disk as baffle plate in the inner tube, about half an inch above the surface of the liquid, to prevent splashing, which may cause an appreciable error in the calculated concentration of the remaining solution at the end of a long series.

The compounds were prepared by crystallising equimolecular proportions of the pure components from alcohol, followed by slow drying in a vacuum over calcium chloride.   Quick drying in a warm atmosphere results in loss of naphthalene. Naphthalene picrate was obtained in golden-yellow needles, m. p. 149·5°. Naphthalene-trinitrotoluene separated as very pale yellow needles, melting persistently at 96·4°, which is a little lower than the value 97—98° given by Hepp (*Annalen*, 1882, **215**, 378).

Results.

In an equilibrium of the type AB $\rightleftharpoons$ A + B, if n represents the total mols. of compound added, and α the fraction dissociated, there are at equilibrium $(1-\alpha)n$ mols. of undissociated compound and αn of each of the two components, the total mols. of solute being $(1 + \alpha)n$. By substituting this last value in Brown and Bury's equation (4), one obtains the expression

$$\Delta t = \Delta t_u + \Delta t_w = k[(1 + \alpha)n + Cn_v]/[(1 + \alpha)n + (C + 1)n_v],$$

where n_v represents mols. of solvent, Δt_u is the observed depression, C and Δt_w are the factors to compensate for the water in solution, and k has the value 55·81.   This leads to

$$\alpha = n_v/n[\{\Delta t/(k - \Delta t)\} - C] - 1 \quad . \quad . \quad . \quad (1)$$

If the concentrations in the mass action equation $K = [A][B]/[AB]$ are again expressed as mol. fractions, we arrive at a value for the equilibrium constant in measurable quantities :—

$$K = \alpha^2 n/[1 - \alpha][(1 + \alpha)n + (C + 1)n_v] \quad . \quad . \quad (2)$$

The results are shown in the accompanying tables, each of which contains the collected data of three independent series. The first column gives the number of grams of compound per 100 grams of solvent (w), Δt_u is the observed depression, α(obs.) and K are calculated from equations (1) and (2). The values of α (calc.) have been obtained from equation (2), assuming the mean value of K.   Taking into account the possible error of 0·003° in the determination of Δt_u, the agreement between the observed and calculated values of α, and the constancy of K, are satisfactory.

The Free Energy of Formation of Naphthalene Picrate.

Naphthalene picrate reaches its solubility limit at a depression (Δt_u) of 2·380°, corresponding to an actual temperature of 2·966°.

TABLE I.

Solute—Naphthalene–trinitrotoluene (Molecular weight = 355·2).

	$\Delta t_{u}.$	α (obs.).	α (calc.).	$K.$
1·0547	0·399°	0·993	0·993	0·524
2·4362	0·907	0·980	0·984	0·394
2·7309	1·014	0·978	0·982	0·408
4·2139	1·545	0·972	0·971	0·485
5·1427	1·863	0·960	0·965	0·392
6·1878	2·227	0·960	0·959	0·467
6·4683	2·319	0·957	0·957	0·455
7·2431	2·578	0·952	0·950	0·454
7·3594	2·620	0·953	0·952	0·471
8·5054	2·995	0·947	0·947	0·468
8·6726	3·057	0·951	0·945	0·525
9·4009	3·290	0·946	0·942	0·504
10·645	3·681	0·937·	0·935	0·506
11·766	4·020	0·927	0·929	0·439
			Mean	0·464

TABLE II.

Solute—Naphthalene picrate (Molecular weight = 357·2).

$w.$	$\Delta t_{u}.$	α (obs.).	α (calc.).	$K.$
2·0664	0·766°	0·977	0·971	0·286
2·1831	0·806	0·970	0·969	0·231
3·3670	1·225	0·956	0·955	0·234
4·2689	1·532	0·942	0·945	0·217
4·6508	1·662	0·941	0·940	0·232
5·3871	1·908	0·929	0·932	0·215
6·0586	2·127	0·925	0·925	0·228
6·3179	2·210	0·916	0·923	0·208
6·7241	2·339	0·909	0·918	0·201
			Mean	0·228

We are thus in a position to calculate its free energy of formation by means of the usual van 't Hoff isotherm :—

$$A = RT \ln N_1 \times N_2/N_3 - RT \ln K,$$

where N_1, N_2, and N_3 represent initial concentrations of components and compound respectively, expressed in the same units, $i.\,e.$, mol. fractions, that were used in determining K, the equilibrium constant. We are concerned with the formation of the solid compound from the solid components. The initial concentrations will therefore be those concentrations at which the solids are in equilibrium with the saturated solution, $i.e.$, their solubilities.

At the solubility limit the picrate is still considerably dissociated, but the solubility, N_3, of the undissociated compound can be obtained direct from the freezing-point readings by plotting the logarithm of its mol. fraction, $(1 - \alpha)n/[(1 + \alpha)n + (C + 1)n_v]$, against the observed depression and making a small extrapolation to 2·380°. This leads to a value of $N_3 = 0·00187$.

N* 2

The limits of solubility of the components are not reached in the range of experiments, but their "ideal" solubilities at the same temperature (3° approx.) may be calculated in mol. fractions by the method of Hildebrand ("Solubility," American Chemical Society Monograph, 1924, p. 37), a justifiable proceeding in view of the fact that it has been shown that they form ideal solutions. Assuming for picric acid a molecular latent heat of fusion of 4160 cals. (Mortimer, *J. Amer. Chem. Soc.*, 1922, **44**, 1416), and a melting point of 122°, N_2 becomes 0·1021. No specific heat data are available, and neglect of these must make the result slightly low. Using the complete thermal data as given by Hildebrand (*op. cit.*), the calculated value of N_1 is 0·1857.

By substituting the above values for N in the van 't Hoff isotherm, and taking $K = 0·228$ as a mean, the free energy of formation of naphthalene picrate at 3° is 2083 cals. per mol. This is in close agreement with values given by Brönsted (*Z. physikal. Chem.*, 1912, **78**, 284) of 2050 cals. at 20·1°, from *E.M.F.* measurements, and of 2150 and 2190 cals. at 0 and 20°, respectively, from solubility data.

LV.—*Constitutional Studies in the Monocarboxylic Acids Derived from Sugars. Part III. The Isomeric Tetramethyl Galactonolactones and Trimethyl Arabonolactones.*

By JOHN PRYDE, EDMUND LANGLEY HIRST, and ROBERT WILLIAM HUMPHREYS.

IN Part I (J., 1923, **123**, 1808), two isomeric tetramethyl *d*-galactonolactones were described—one, prepared by methylation of *d*-galactonolactone, had a lævorotation of − 29·5° and, it was suggested, a 1 : 4-structure, whilst the other, obtained by the oxidation of tetramethyl *d*-galactose, had a dextrorotation of + 106·7°. To this a 1 : 5-structure was assigned. Levene and Meyer (*J. Biol. Chem.*, 1924, **60**, 167), using the same methods, prepared two isomeric tetramethyl mannonolactones, both isomerides possessing in this

case dextrorotations,* as would be expected according to the Hudson rule (*J. Amer. Chem. Soc.*, 1910, **32**, 338), if 1 : 4- and 1 : 5-structures are ascribed to these lactones. The present communication deals with further observations on these tetramethyl galactonolactones, and with an extension of the investigations which reveals a similar isomerism of trimethyl *l*-arabonolactone.

Fischer (*Ber.*, 1895, **28**, 1154) has shown that the action of dry methyl-alcoholic hydrogen chloride on galactose produces at least one other form of methyl galactoside in addition to the well-characterised α- and β-forms of the normal methyl hexoside. Irvine and Cameron (J., 1905, **87**, 900) showed that this additional form or forms may be converted on methylation into a tetramethyl methylgalactoside isomeric with the normal tetramethyl α- and β-methyl-*d*-galactosides, and that on hydrolysis the abnormal form gave rise to a tetramethyl *d*-galactose with a much lower dextro-rotation than that obtained from the normal α- and β-forms. Later, Miss Cunningham (J., 1918, **113**, 596) correlated this third form with the reactive " γ " series of sugars.

With the view of eliminating complications dependent on the formation of such reactive types, we have made use, in certain of our investigations, of the process of Haworth (J., 1915, **107**, 8), in which the free sugar is methylated directly by methyl sulphate and caustic soda. Nevertheless, when the total product from this process was converted into tetramethyl galactose, the equilibrium rotation of the latter in water was well below that quoted by previous workers (compare Irvine and Cameron, J., 1904, **85**, 1071; Schlubach and Moog, *Ber.*, 1923, **56**, [*B*], 1957). The tetramethyl galactose used in the previous work (Part I, *loc. cit.*) was obtained by this direct methylation process and showed [α]$_D$ + 84·9° in water. It was recognised at the time that this value was below the standard values already quoted, but no explanation of the anomaly was then forthcoming, since the method used in preparing the methylated sugar was known to give, when applied to glucose, a homogeneous tetramethyl glucose showing the normal rotation. The question has now been further investigated, and the fact that direct methylation of galactose with methyl sulphate yields a tetramethyl galactose with a specific rotation well below the normal value has been substantiated : the explanation would appear to be that during the first stages of the methylation, while the reducing group is being substituted, isomeric methyl galactosides

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* Levene and Meyer (*loc. cit.*, 168) say, " It is peculiar that the two tetra-methyl lactones should rotate in opposite directions. This peculiarity requires elucidation." This is obviously in error, the statement presumably referring to the acids.

are formed containing respectively the 1 : 5- and 1 : 4-oxide linking. On further methylation these give rise to a mixture of tetramethyl methylgalactosides containing the amylene-oxidic form in excess.* Thus utilising as initial material a homogeneous tetramethyl galactose ($[\alpha]_D^{18°} + 117 \cdot 3°$ in water), which had in turn been prepared from crystalline α-methyl-d-galactoside, we have obtained a tetramethyl galactonolactone with a much higher dextrorotation than that previously quoted for the 1 : 5-isomeride, namely, 160·7° in place of 106·7°. From the evidence now at our disposal, we believe that the higher value must be assigned to the pure 1 : 5-isomeride of the lactone and that the previously described dextrorotatory lactone is not a homogeneous form, but is to be regarded as a mixture of the 1 : 5 and 1 : 4 forms. Similar anomalous rotations—in this case lower still—have been observed when tetramethyl galactose and the corresponding lactone have been prepared from the mixed methylgalactosides obtained from Fischer's acid methyl alcohol process. Here the proportion of 1 : 4 form in the mixture is greater than can be obtained by direct methylation with methyl sulphate. From certain preparations of these mixed lactones a crystalline tetramethyl galactonamide has been obtained. The yield of recrystallised material and the result of the action of alkaline hypochlorite on the amide (compare Irvine and Pryde, 1924, **125**, 1045) are such that further support is gained for the view that the original sugars and the lactones and amides prepared from them were mixtures of the 1 : 5- and 1 : 4-isomerides. The reaction of the pure isomeric amides is now being studied.

A parallel series of investigations on the corresponding derivatives of l-arabinose gave results similar to those encountered in the case of galactose. Starting from crystalline trimethyl α-methyl-l-arabinoside, a *dextrorotatory* trimethyl arabonolactone has been obtained having an initial specific rotation in water (15 minutes after solution) of + 138°, falling in the course of 24 hours to + 22·4°. This must be regarded as a homogeneous form, and since Hirst and Robertson (following paper) have obtained evidence which establishes the presence of the 1 : 5 type of oxide linking in *normal*, fully methylated arabinose, it follows that the new lactone also possesses the 1 : 5-oxide linking. It is evident from a study

* In a recent communication by Haworth, Ruell, and Westgarth (J., 1924, **125**, 2468), which appeared after the present paper had been sent in for publication, the isolation of the 1 : 4-oxidic form of tetramethyl galactose and the corresponding lactone is described, and it is pointed out that our original preparation of 1 : 5-tetramethyl galactonolactone contained an admixture of the 1 : 4 form. As is clear from the results now described, we are in complete agreement with Haworth and his collaborators both as regards his correction of the earlier work and his deductions therefrom.—J. P.

of the valency configuration in a compound of this type that the oxide ring, although attached at one end to a non-asymmetric, terminal carbon atom, must be definitely oriented either to the right- or to the left-hand side of the carbon chain, and the application of Hudson's rule (*loc. cit.*) shows that in this trimethyl arabonolactone the ring is on the right of the carbon chain. It is also of interest to compare the dextrorotation of this methylated lactone with the lævorotation of the non-methylated arabonolactone obtained by direct oxidation of the free sugar, a case quite parallel to that of the galactose derivatives. Experiments are in progress with the view of obtaining the pure lævorotatory isomeride of the methylated lactone by the method previously utilised for the preparation of the lævorotatory isomeride of tetramethyl galactonolactone.

On subjecting *l*-arabinose to the action of dry hydrogen chloride in methyl alcohol, followed by methylation of the mixed arabinosides, the trimethyl arabinose obtainable has an equilibrium rotation in water well below that found by Purdie and Rose, + 127·2° (J., 1906, 89, 1204), and the trimethyl arabonolactone obtained from this sugar on oxidation likewise has a rotation much below that of the homogeneous 1 : 5-lactone already described. Further, preparations of mixed arabinosides which, when hydrolysed and oxidised with bromine, give rise to trimethyl arabonolactones with anomalous low rotations, also behave in an anomalous way when oxidised with nitric acid. In place of dimethyl trimethoxyglutarate, there was obtained a mixture of this compound with what is apparently the lactone of a monocarboxylic acid, presumably the 1 : 4-trimethyl arabonolactone, and the yield of trimethoxyglutardiamide obtained from this mixture is in agreement with these views as to its composition. In our opinion, these results point to the existence of isomeric arabinoses and arabonolactones with 1 : 5- and 1 : 4-oxygen bridges, and to the fact that a mixture of the isomeric sugars is obtained on treating arabinose with acid methyl alcohol.

It is of great interest that galactose and arabinose exhibit this marked tendency to react in both 1 : 5- and 1 : 4-forms— the former being the normal form in both cases—under conditions which, so far as our own observations and those of other workers go, lead to the production of only one form in the cases of glucose

H OH		H OH	
HO H	H OH	HO H	H OH
HO H	HO H	H OH	HO H
H OH	HO H	H OH	H OH
Galactose.	Arabinose.	Glucose.	Xylose.
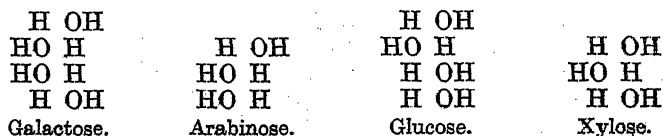
and xylose. In this respect, the relationships between the formulæ of galactose and arabinose on the one hand, and between those of glucose and xylose on the other hand, are suggestive.

EXPERIMENTAL.

1:5-*Tetramethyl* d-*Galactonolactone.*—Pure, recrystallised α-methyl-galactoside monohydrate ($[\alpha]_D^{16°} + 177°$ for $c = 0.871$; Fischer, *loc. cit.*, gives $[\alpha]_D^{20°} + 179°$) was methylated in the usual way with methyl sulphate and sodium hydroxide followed by two treatments with methyl iodide and silver oxide. The fully methylated product after distillation had $n_D^{17°}$ 1.4505, and on being heated for 5 hours at 100° in 3% methyl-alcoholic hydrogen chloride in a sealed tube, it had the equilibrium rotation $[\alpha]_D^{22°} + 96.5°$ ($c = 0.728$). Hydrolysis by 8% aqueous hydrochloric acid produced a viscous syrup which, after distillation, had $n_D^{17°}$ 1.4633, and $[\alpha]_D^{18°} + 117.3°$ ($c = 0.996$; equilibrium rotation in water). The tetramethyl galactose was oxidised with bromine (see Part I, *loc. cit.*), and the resulting tetramethyl galactonolactone, which distilled at 112—116°/0.57 mm. as a mobile syrup, had $n_D^{17°}$ 1.4574, and showed in water ($c = 1.086$) $[\alpha]_D^{17.7°} + 160.67°$ (5 minutes after the preparation of the solution), $[\alpha]_D^{17.9°} + 72.54°$ (after 4.5 hours), and $[\alpha]_D^{18.3°} + 47.58°$ (after 20 hours : constant) [Found : C = 51.08; H = 7.84; OMe = 52.7. Calc. for $C_6H_6O_2(OMe)_4$, C = 51.28; H = 7.69; OMe = 53.0%]. On titration, the typical behaviour of a lactone was observed, 0.1162 g. requiring for complete neutralisation 4.96 c.c. of $N/10$-sodium hydroxide (calc., 4.88 c.c.).

The Direct Methylation of Galactose by Methyl Sulphate and Sodium Hydroxide.—Galactose ($[\alpha]_D^{16°}$ in water $+ 143.1°$ for $c = 1.22$; $[\alpha]_D^{16°} + 80.84°$ after 18 hours) was methylated at 30° in the customary manner, until no reducing action on Fehling's solution could be detected. After repetition of the process, the fully methylated product, separated by fractional distillation in a vacuum, had no action on alkaline or neutral permanganate. The tetramethyl methylgalactoside [Found : OMe = 60.5. Calc. for $C_6H_7O(OMe)_5$, OMe = 62.0%] was hydrolysed by boiling for 30 minutes with 8% aqueous hydrochloric acid, and the product isolated as a viscous syrup. On fractional distillation in a vacuum, this gave a considerable residue of high b. p. and a main fraction (b. p. 130°/0.3 mm.) of tetramethyl galactose [Found : C = 50.83; H = 8.55; OMe = 50.8. Calc. for $C_6H_8O_2(OMe)_4$, C = 50.85; H = 8.47; OMe = 52.1%], which showed $n_D^{15°}$ 1.4618, $[\alpha]_D + 83.3°$ ($c = 1.799$) in water, $+ 57°$ ($c = 1.535$) in alcohol, and $+ 65°$ ($c = 1.401$) in benzene. In duplicate experiments, products were

obtained with physical constants almost identical with those recorded above.

Tetramethyl Galactonamide.—A dry alcoholic solution of tetramethyl galactonolactone ([α] $+ 106 \cdot 7°$; prepared from tetramethyl galactose obtained by direct methylation as described above) was treated with ammonia as described by Irvine and Pryde (*loc. cit.*). The product crystallised after 4—5 days, and, on recrystallisation from light petroleum (b. p. 60—80°) containing a little ethyl alcohol and ether, gave tetramethyl galactonamide, m. p. 121°, [α]$_D^{9 \cdot 3°}$ $+ 35 \cdot 7°$ ($c = 0 \cdot 937$) in acetone (yield about 25% of the crude product) [Found : C $= 47 \cdot 68$; H $= 8 \cdot 27$; OMe $= 47 \cdot 7$. Calc. for $C_6H_9O_2N(OMe)_4$, C $= 47 \cdot 81$; H $= 8 \cdot 37$; OMe $= 49 \cdot 4\%$]. On treating the crude amide with an alkaline hypochlorite solution according to Weerman's method, a small yield was obtained of a crystalline, nitrogenous substance, which softened at 140°, melted at 150°, and had [α]$_D$ $+ 85 \cdot 7°$ ($c = 0 \cdot 998$) in water, falling to $+ 27 \cdot 5°$ after the substance had been treated with 3% hydrochloric acid at room temperature for 3 days. This compound is evidently analogous to the cyclic urethane resulting from the action of alkaline hypochlorite on tetramethyl gluconamide (Irvine and Pryde, *loc. cit.*), but from the poor yields it is inferred that the original amide is not a homogeneous product.

Since the parent lactone must be regarded as a mixture of the 1 : 5- and 1 : 4-isomerides, the structures of the amide and of the compound derived from it are not yet clear, although at present we incline to the view that the latter is derived from the amide obtained from the 1 : 4-lactone. The matter is being further investigated.

Methylation of Galactose with Preliminary Galactoside Formation in Methyl-alcoholic Hydrogen Chloride and the Preparation of Mixed Tetramethyl Galactonolactones.—In the following series of experiments the galactose was dissolved in 1% methyl-alcoholic hydrogen chloride, and heated in sealed tubes for 20 hours at 100°. The mixed galactosides were then methylated with methyl sulphate and sodium hydroxide followed by methyl iodide and silver oxide. The fully methylated product distilled steadily at 104·8— 105·0°/0·48—0·52 mm., and had $n_D^{8 \cdot 6°}$ $1 \cdot 4500$ and $n_D^{12 \cdot 6°}$ $1 \cdot 4484$ [Found : OMe $= 60 \cdot 3$; calc., $62 \cdot 0\%$]. On hydrolysis, an 88% yield of crude tetramethyl galactose was obtained, the bulk of which, on fractional distillation, showed b. p. 140°/1·0—1·2 mm., $n_D^{13°}$ $1 \cdot 4620$, and [α]$_D$ $+ 70°$ in water (equilibrium value) [Found : C $= 50 \cdot 50$; H $= 8 \cdot 43$; OMe $= 51 \cdot 2\%$]. A quantity of high-boiling residue remained. On oxidation with bromine, the above preparation of tetramethyl galactose gave a tetramethyl galactono-

lactone [Found : C = 51·30 ; H = 7·73 ; OMe = 52·6%], which could be further fractionated as follows without appreciably affecting the analytical figures :

I. $n_D^{15°}$ 1·4546; $[\alpha]_D^{17·6°}$ +61·7°, falling in 24 hours to $[\alpha]_D^{18°}$ +2·38° (c = 1·066).
II. $n_D^{15°}$ 1·4538; $[\alpha]_D^{19°}$ +48·75°, falling in 24 hours to $[\alpha]_D^{19°}$ −0·39° (c = 1·077)·

The behaviour of the lactone on titration was typical, 0·2120 g. requiring 8·8 c.c. of N/10-sodium hydroxide for complete neutralisation (calc., 9·06 c.c.). The following table records the initial specific rotations in water (a), and the refractive indices of various preparations of tetramethyl galactonolactones, all of which gave good analytical figures. It will be seen that the constants vary more or less in the same sense, which lends support to the view that the mixed forms of intermediate rotation consist of varying proportions of the 1 : 5- and 1 : 4-isomerides.

Tetramethyl Galactonolactones.

$a.$	$n_D^{15°}.$	Notes.
+160°	1·4582	1 : 5-Form prepared from homogeneous tetramethyl d-galactose.
+106	1·4571	From a preparation of tetramethyl galactose obtained by direct methylation of galactose with Me_2SO_4.
+ 61	1·4546	From preparations of tetramethyl galactose obtained by preliminary HCl/MeOH treatment of galactose.
+ 48	1·4538	
− 29	1·4496	1 : 4-Form prepared by methylation of d-galactonolactone.

1 : 5-*Trimethyl* l-*Arabonolactone*.—The initial material was crystalline trimethyl α-methyl-*l*-arabinoside having $[\alpha]_D^{17·5°}$ + 225·3° in methyl alcohol (c = 1·308) and $[\alpha]_D^{18°}$ + 246·1° in water (c = 0·723), which had been prepared from recrystallised α-methyl-*l*-arabinoside by methylation with methyl iodide and silver oxide. In various preparations of trimethyl arabonolactone considerable difficulty was experienced, during the acid hydrolysis necessary for the preparation of the free sugar, owing to the large amount of the methylated sugar which was decomposed with the formation of furfural. This difficulty was overcome by the following process of simultaneous hydrolysis and oxidation. A solution of the crystalline trimethyl methylarabinoside (7·7 g.) in 3% aqueous hydrobromic acid (85 c.c.), having been maintained at 85° for 1 hour, was treated at 75° with small quantities of bromine at intervals of 30 minutes, until, after 4 hours, 3·5 c.c had been added. After standing for 24 hours at room temperature, the solution was again heated at 75° and a further 5 c.c. of bromine were added (making a total of 3 mols.). The excess of bromine was then removed by aeration, the hydrobromic acid neutralised with silver oxide, the

filtered solution saturated with hydrogen sulphide, and the clear filtrate from the precipitated silver sulphide was evaporated under diminished pressure to a syrup, which was dissolved in chloroform to remove some inorganic matter still present. The syrup finally obtained (6·6 g.) was heated at 100°/9 mm. for 2 hours to ensure complete conversion of the acid into the lactone. Distillation in a vacuum then gave 5·15 g. of product, b. p. 156°/12 mm., $n_D^{15°}$ 1·4595, and a second fraction (0·2 g.), b. p. 158°/12 mm., $n_D^{15°}$ 1·4592. The still residue weighed only 0·3 g. The main fraction was a colourless syrup with a wide range of solubility in organic solvents, acid to litmus, and showing the characteristic behaviour of a lactone. It did not reduce Fehling's solution, even on prolonged boiling. Analysis established its identity as trimethyl arabono-lactone [Found : C = 50·23; H = 7·45; OMe = 48·7. Calc. for $C_5H_5O_2(OMe)_3$, C = 50·53; H = 7·37; OMe = 48·9%]. 0·1529 G. of the lactone required 8·1 c.c. of $N/10$-sodium hydroxide for complete neutralisation (calc., 8·05 c.c.), the substance behaving as an easily hydrolysable lactone. In ethyl alcohol, the $[\alpha]_D + 136°$ ($c = 1·830$) remained constant. In water, the initial high $[\alpha]_D^{18°} + 145°$ (by extrapolation) fell in 15 minutes to $+ 138°$, in 1 hour to $+ 112°$, in 2·5 hours to $+ 55·7°$, in 7 hours to $+ 23·6°$, and in 24 hours to $+ 22·4°$ (constant). On the assumption that the lactone is completely converted into the acid, the latter value corresponds to $[\alpha]_D^{18°} + 20·4°$ for trimethyl arabonic acid. For comparative purposes, the latter constant was also determined as follows. 0·1356 G. of the lactone, dissolved in a small quantity of water, was treated with rather more than the necessary amount of sodium hydroxide to form the sodium salt of the acid, ample time being given for the change to take place. A slight excess of hydrochloric acid was then added, the volume made up to 10 c.c. with water, and the specific rotation determined with the minimum possible delay (50 seconds from the time of adding the acid). The value of $[\alpha]_D^{18°}$ found in this way was constant ($+ 22·9°$, $c = 1·485$ as acid). It would therefore appear that in water 1 : 5-trimethyl arabonolactone is completely converted into the acid. Confirmation of this was obtained by titrating with alkali an aqueous solution of the lactone which had been kept for several hours. The behaviour then observed was that of an acid, the titration proceeding at once to a sharp and permanent end-point (0·0980 g. required 5·0 c.c. of $N/10$-sodium hydroxide. Calc., 5·0 c.c.). Neither the acid nor the lactone could be obtained in a crystalline condition. The salts of the acid are very soluble in water, the solubilities of the sodium, potassium, ammonium, barium, lead, and mercury salts being such that they are not precipitated even

from moderately concentrated solutions. 1 : 5-Trimethyl arabono-
lactone forms a crystalline amide (m. p. 95—100°) on saturating
its solution in methyl alcohol with dry ammonia.

*Methylation of Arabinose with Preliminary Arabinoside Formation
in Methyl-alcoholic Hydrogen Chloride and the Preparation of Mixed
Trimethyl Arabonolactones.*—A typical preparation is described.
5·5 G. of arabinose was treated with methyl alcohol containing
0·2% of hydrogen chloride in a sealed tube at 105° for 24 hours.
The partly crystalline product had no action on Fehling's solution.
The mixture of syrup and crystals was methylated twice with methyl
sulphate and sodium hydroxide, and the resulting mobile syrup
was distilled, giving trimethyl methylarabinoside as the main
fraction (2 g.), b. p. 120°/13 mm., $n_D^{15°}$ 1·4448 [Found : C = 52·50;
H = 8·80; OMe = 58·1. Calc. for $C_5H_6O(OMe)_4$, C = 52·42;
H = 8·74; OMe = 60·2%]. It was neutral to litmus, behaved as
a normal stable glucosidic compound, and had no action on neutral
or slightly alkaline potassium permanganate solution. $[\alpha]_D + 79\cdot6°$
($c = 3\cdot332$) in methyl alcohol. After being heated in acid methyl
alcohol in a sealed tube for 8 hours at 90°, the substance gave as
equilibrium value $[\alpha]_D + 60°$, a figure much below that given by
crystalline preparations of the α- and β-forms of normal trimethyl
methylarabinoside (+ 150°, Hirst and Robertson, *loc. cit.*). In
certain other preparations, the mixed arabinosides were methylated
with methyl iodide and silver oxide, and also with the latter reagents
following a preliminary treatment with methyl sulphate and sodium
hydroxide. In all cases, abnormal rotations were recorded for the
trimethyl methylarabinosides, and for the trimethyl arabinose and
arabonolactones prepared from them. The following results are
typical :

Series I. The mixed arabinosides were methylated with methyl
iodide and silver oxide; the fully methylated product was hydro-
lysed with 8% aqueous hydrochloric acid, and the trimethyl
arabinose oxidised by bromine. During the hydrolysis, very
considerable furfural formation occurred. The trimethyl methyl-
arabinoside (Found : OMe = 59·0; calc., 60·2%) had $[\alpha]_D + 79°$
in water, whilst the trimethyl arabinose (Found : OMe = 47·9;
calc., 48·4%) had as equilibrium value in water $[\alpha]_D + 36\cdot2°$. The
trimethyl arabonolactone (Found : C = 50·13; H = 7·02; OMe =
48·6%), b. p. 80—90°/0·2—0·4 mm., behaved typically on titration,
0·1393 g. requiring 7·8 c.c. of $N/10$-sodium hydroxide (calc., 7·33 c.c.).
$[\alpha]_D$ in water + 17·45° (initial value), and − 20·95° (constant value)
after 24 hours.

Series II. The mixed arabinosides were methylated by methyl
sulphate and sodium hydroxide, followed by methyl iodide and

silver oxide; the fully methylated product was simultaneously hydrolysed and oxidised by a mixture of hydrobromic acid and bromine as described above. The trimethyl methylarabinoside had $[\alpha]_D + 59 \cdot 8°$ in water, whilst the lactone obtained from it showed in water $[\alpha]_D + 55 \cdot 8°$ (initial value) and $- 13 \cdot 9°$ (after several hours).

Oxidation of Mixed Trimethyl Methylarabinosides with Nitric Acid.—The material (1·3 g.), prepared by methylation of mixed methylarabinosides with methyl sulphate and sodium hydroxide, was dissolved in 45 c.c. of nitric acid (d 1·2) and the oxidation was carried out by Hirst and Robertson's method (*loc. cit.*), the products being isolated as methyl esters. The colourless syrup so obtained (1·3 g.) gave on distillation 1·1 g., b. p. 155—160°/22—23 mm., $n_D^{14°}$ 1·4392. The main fraction was a colourless syrup, soluble in water and all the usual organic solvents, which showed the properties of a lactone or easily hydrolysable ester. It appeared not to be a single substance, but was shown to contain dimethyl trimethoxyglutarate, since it gave a 20% yield of the crystalline diamide (m. p. 233°) when treated with ammonia in methyl alcohol (compare Hirst and Robertson, *loc. cit.*) (0·2 g., dissolved in 2 c.c. of methyl alcohol saturated at 0° with ammonia, gave crystals in 48 hours, the final yield of pure material being 0·04 g.). On analysis figures were obtained which support the view that the product consisted of a mixture of dimethyl trimethoxyglutarate, $C_5H_3O_2(OMe)_5$, and trimethyl arabonolactone, $C_5H_5O_2(OMe)_3$,—presumably the 1 : 4-form. The results are tabulated below :

	Found.	Calc. for $C_5H_3O_2(OMe)_5$ (A).	Calc. for $C_5H_5O_2(OMe)_3$ (B).	Calc. for 50%A+50%B.
C%	49·2	48·0	50·5	49·25
H%	7·4	7·2	7·4	7·3
OMe%	56	62	49	55·5
C.c. of N/10-sodium hydroxide required to hydrolyse 0·1 g.	6·7	8	5·2	6·6

$[\alpha]_D + 25 \cdot 8°$ ($c = 1 \cdot 430$) in methyl alcohol; $[\alpha]_o + 22°$ ($c = 0 \cdot 820$), final value in water.

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LVI.—*The Constitution of the Normal Monosaccharides. Part II. Arabinose.*

By EDMUND LANGLEY HIRST and GEORGE JAMES ROBERTSON.

As the result of recent discoveries concerning the nature of the oxide-ring linking in carbohydrates, still greater emphasis must be laid on the necessity of obtaining for each individual sugar independent evidence as to internal structure. Thus, for example, an examination of derivatives chosen both from the normal and from the γ-type of compounds has revealed the fact that the same 1 : 5-oxide linking is present in tetramethyl γ-fructose (Haworth and Linnell, J., 1923, **123**, 294) and in the normal sugars trimethyl xylose (Hirst and Purves, *ibid.*, 1352) and tetramethyl galactose (Pryde, *ibid.*, 1808), whilst evidence pointing to a similar structure for normal tetramethyl mannose has also been obtained (Levene and Meyer, *J. Biol. Chem.*, 1924, **60**, 167). In the case of galactose, it is of special interest to find that the γ-derivative is of the 1 : 4- or butylene-oxidic structure (Haworth, Ruell, and Westgarth, J., 1924, **125**, 2468). These investigations have now been supplemented by inquiries into the structure of normal and γ-derivatives of the pentose sugar arabinose, and the following interesting conclusions have been drawn. Derivatives of the γ-series of arabinose compounds have been found by Baker and Haworth (an account of whose experiments we have been privileged to receive from the authors prior to publication) to contain the 1 : 4- or butylene-oxidic linking (following paper), and, on the other hand, normal stable derivatives of arabinose have been shown by us to be definitely of the amylene-oxidic or 1 : 5-type.

As a preliminary to work on the constitution of arabinose, a further study of the methylation of this sugar has been carried out, leading to the discovery of trimethyl β-methylarabinoside (compare Purdie and Rose, J., 1906, **89**, 1204). This compound (m. p. 46—48°), which was prepared by methylating the free sugar with methyl sulphate, has the properties of a normal stable glucoside. Polarimetric studies of the hydrolysis of the new compound, along with determinations of the equilibrium value of the specific rotation in acid methyl alcohol, indicate that the same type of oxide linking is present in this sugar and in Purdie's trimethyl α-methylarabinoside, and that these substances bear to each other the relationship of interconvertible α- and β-varieties of normal trimethyl methylarabinoside. The equilibrium value of the specific rotation of the liquid trimethyl methylarabinosides formed simultaneously with this new modification indicates the presence of isomerides containing

a different oxide-ring structure. The behaviour of arabinose is here parallel to that of galactose, which under similar conditions of methylation yields a mixture of methylated products containing respectively the 1 : 4- and the 1 : 5-oxide linkings (Pryde, Hirst and Humphreys, preceding paper).

Information concerning the internal structure of the normal derivatives of arabinose has been gained from a study of the oxidation by nitric acid of the fully methylated trimethyl arabinose (III), derived from the crystalline trimethyl α-methylarabinoside (II). The sole oxidation product, which was isolated in almost quantitative yield, was trimethoxyglutaric acid (IV). Special precautions were taken to prevent methylation of free hydroxy-groups. It is thus evident that, when the normal form of fully methylated arabinose is oxidised under the conditions here adopted, it gives rise to a dibasic acid which still contains a chain of five carbon atoms and has been formed without loss of any of the methoxyl groups present in the original trimethyl arabinose. By arguments similar to those advanced in the previous paper on xylose, these observations can be interpreted only as showing that the structure of the normal form of fully methylated arabinose is of the amylene-oxide type (II). The detailed study of the methylation process as applied to sugars which has been carried out during the past few years goes to show that the oxide linking of a normal methylaldoside remains unaltered during methylation, and therefore it follows that the unsubstituted α- and β-methylarabinosides from which the fully methylated derivatives are prepared also contain this type of oxide linking. These experiments, although not in themselves affording direct evidence concerning the structure of the free sugar, may be considered in conjunction with arguments based on a comparison of the optical properties and the general reactions of free arabinose with the corresponding properties of the normal and γ-forms of methylarabinoside. They then lend strong support to the view that the same internal structure is present in the free aldose and in the normal forms of methylarabinoside and their methylated derivatives. We therefore consider that the behaviour of arabinose may best be understood at the present time on the basis of the amylene-oxidic ring structure (I) (compare Hirst and Purves, loc. cit.).

One point—which, however, does not in any way affect the validity of the preceding arguments—requires to be considered in somewhat greater detail. The work described has been carried out with l-arabinose, which has been found to yield a dimethyl trimethoxyglutarate with marked dextrorotatory powers. It is evident that this ester and the dimethyl trimethoxyglutarate obtained by

Haworth and Linnell from tetramethyl γ-fructose (a sugar belonging to the d-series) should be optical enantiomorphs, but these authors have found (*loc. cit.*) that their product also is dextrorotatory, almost to the same degree as our own. The rotations shown by our materials have been confirmed on several occasions with samples of different origin, and in these circumstances it was felt that a further examination of the question of optical activity was necessary. The most convenient means of attack appeared to lie in the preparation of arabotrimethoxyglutaric acid by an entirely independent method, and this was accomplished by methylating the lævorotatory arabotrihydroxyglutaric acid, $CO_2H\cdot[CH\cdot OH]_3\cdot CO_2H$ (Kiliani, *Ber.*, 1888, **21**, 3007; Fischer, *Ber.*, 1891, **24**, 1844). The methylated product was dextrorotatory, and identical in every respect with the ester derived from methylated arabinose (V); and further proof of the identity of the two compounds was afforded by the isolation of the same crystalline diamide (VI) (m. p. 233°, $[\alpha]_D + 50°$) from both. The increase of the specific rotation in the dextro sense occasioned by methylation is here of the same order $(+ 70°)$ as that found when d-tartaric acid is converted into dimethyl dimethoxysuccinate $(CO_2Me\cdot[CH\cdot OMe]_2\cdot CO_2Me)$, and such a change would appear to be general in this series of dibasic acids. Confirmation of the accuracy of our former observations was thus obtained and further experiments are now in progress by which it is hoped to obtain an explanation of the interesting anomaly in the direction of the optical rotation of the two esters.

$$
\begin{array}{cccccc}
\left[\begin{array}{l} CH\cdot OH \\ CH\cdot OH \\ O\ CH\cdot OH \\ CH\cdot OH \\ CH_2 \end{array}\right. &
\left[\begin{array}{l} CH\cdot OMe \\ CH\cdot OMe \\ O\ CH\cdot OMe \\ CH\cdot OMe \\ CH_2 \end{array}\right. &
\left[\begin{array}{l} CH\cdot OH \\ CH\cdot OMe \\ O\ CH\cdot OMe \\ CH\cdot OMe \\ CH_2 \end{array}\right. &
\begin{array}{l} CO_2H \\ CH\cdot OMe \\ CH\cdot OMe \\ CH\cdot OMe \\ CO_2H \end{array} &
\begin{array}{l} CO_2Me \\ CH\cdot OMe \\ CH\cdot OMe \\ CH\cdot OMe \\ CO_2Me \end{array} &
\begin{array}{l} CO\cdot NH_2 \\ CH\cdot OMe \\ CH\cdot OMe \\ CH\cdot OMe \\ CO\cdot NH_2 \end{array} \\
(I.) & (II.) & (III.) & (IV.) & (V.) & (VI.)
\end{array}
$$
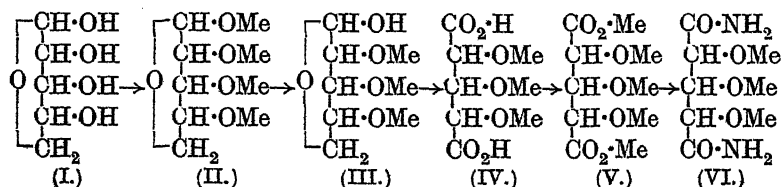
EXPERIMENTAL.

Methylation of Arabinose.—Trimethyl α-methylarabinoside, [*] prepared according to Purdie and Rose (*loc. cit.*) and recrystallised several times, had m. p. 44—46°; $[\alpha]_D + 250°$ in water ($c = 1\cdot200$), $[\alpha]_D + 223°$ in methyl alcohol ($c = 1\cdot320$) (compare Purdie and Rose); $n_D^{30°}\ 1\cdot4432$, $n_D^{25°}\ 1\cdot4450$, the readings being for superfused material.

Trimethyl β-methylarabinoside was obtained by methylating

* We are indebted to Mr. R. W. Humphreys, of the University College of South Wales, Cardiff, for a specimen of very pure trimethyl α-methylarabinoside.

arabinose (10 g.) with methyl sulphate (50 c.c.) and sodium hydroxide (40 g. in 85 c.c. of water) in the usual manner (Haworth, J., 1915, **107**, 8). When the operation was conducted slowly, the formation of coloured by-products was entirely avoided and after one methylation a mobile, colourless syrup (9 g.) was obtained; this, subjected once again to the same treatment, gave 8·5 g. of a syrup, which was purified by distillation. The main fraction (5·5 g., b. p. 123°/24 mm., $n_D^{17°}$ 1·4473) crystallised slowly in long, white needles, which were drained on porous tile. The new product was soluble in all the ordinary organic solvents, including light petroleum, and a suitable medium for recrystallisation could not be found. Purification was effected by the somewhat wasteful method of repeatedly rubbing the crystals with light petroleum and draining rapidly on porous tile, until constancy was attained in the m. p., 46—48°, and rotations : $[\alpha]_D + 24°$ in methyl alcohol ($c = 1·100$), $[\alpha]_D + 46·2°$ in water ($c = 0·865$). The crystals showed all the properties of a typical glucoside and were stable in the presence of neutral or slightly alkaline potassium permanganate solution (Found : C = 52·3; H = 8·8; OMe = 59·8. Required, C = 52·4; H = 8·74; OMe = 60·2%).

Interconversion of the α- and β-Forms of Trimethyl Methylarabinoside.—The initial specific rotation of the α-compound in methyl alcohol was + 223° ($c = 1·563$), whilst the final value, obtained after heating the solution in a sealed tube with the addition of a trace of dry hydrogen chloride, was + 150°. The β-variety, on the other hand, showed initially in acid methyl alcohol $[\alpha]_D + 24°$ ($c = 1·100$), increasing to a final, steady value, + 148°. Further evidence concerning the relationship between these two substances was obtained from a study of the hydrolysis of the β-form with hydrochloric acid. In 8% aqueous acid, the initial value $[\alpha]_D + 47·6°$ ($c = 1·572$) was observed. On heating the solution at 90°, the specific rotation increased regularly to a maximum constant value, + 146° ($c = 1·469$), which is in good agreement with the figure, + 153°, quoted by Purdie and Rose as the end value in the hydrolysis of pure trimethyl α-methylarabinoside. The value quoted is somewhat higher than those found by these authors during a study of the hydrolysis of mixtures containing both the α- and the β-form, and higher also than the figure found for trimethyl arabinose itself (+ 127°), but this discrepancy may be connected with the failure of the syrupy trimethyl arabinose from which Purdie and Rose prepared the mixtures of the α- and β-forms of the fully methylated methylarabinoside, to give satisfactory analytical results (*loc. cit.*).

It is apparent, therefore, that these two crystalline substances

are interconvertible α- and β-varieties of the same trimethyl methylarabinoside. On the other hand, the initial specific rotation, $[\alpha]_D + 57\cdot4°$ ($c = 3\cdot708$), of the analytically pure mixture of crystals and syrup forming the whole of the fully methylated arabinose (material described above as the main fraction) increased in acid methyl alcohol to an equilibrium value, $+ 129°$, and on hydrolysis the final value was observed to be $+ 110°$. These figures are considerably lower than those given by the pure crystalline α- and β-forms, and may be taken as indicating that during the methylation process a quantity of material had been formed differing in internal structure from the normal trimethyl methylarabinoside. Similar observations were made during a study of the methylation of galactose (Pryde, Hirst, and Humphreys, *loc. cit.*).

Simultaneous Hydrolysis and Oxidation of Trimethyl α-Methylarabinoside. Isolation of Methyl Trimethoxyglutarate (V).—In a typical oxidation experiment, a solution of trimethyl α-methylarabinoside (1·90 g.) in nitric acid (d 1·2) (45 c.c.) was heated at 90° for 6 hours, until the oxidation was complete. The excess of nitric acid having been removed (for details, see Hirst and Purves, J., 1923, **123**, 1357), the oxidation product was boiled with 3% methyl-alcoholic hydrogen chloride, the acid neutralised with silver carbonate in the cold, a quantity of anhydrous sodium sulphate added to take up any water, and the solvent distilled from the filtered solution under diminished pressure. The residual syrup was freed from a small quantity of silver nitrate by dissolution in chloroform, and, finally, a colourless, mobile liquid (2·1 g.) was isolated which gave on distillation 1·90 g., b. p. 143°/18 mm., $n_D^{21°}$ 1·4355 (yield 83% of the calculated quantity). A further 0·10 g., b. p. 145—150°/16 mm., $n_D^{17°}$ 1·4385, was obtained as a second fraction, and the still residue remained uncoloured and weighed less than 0·10 g. The main fraction was *methyl arabotrimethoxyglutarate*, a colourless, refractive, moderately mobile, uncrystallisable syrup, soluble in water and in all the usual organic solvents (Found : C = 48·0 ; H = 7·33 ; OMe = 60·2 ; CO_2Me, by quantitative hydrolysis with $N/10$-NaOH, = 48·1. $C_{10}H_{18}O_7$ requires C = 48·0 ; H = 7·24 ; OMe = 62·0 ; CO_2Me = 47·2%). In methyl alcohol, the ester showed $[\alpha]_D + 47\cdot3°$ ($c = 1\cdot842$) and in water $[\alpha]_D + 45°$ ($c = 1\cdot462$).

Trimethoxyglutardiamide (VI).—From a mixture of the ester (0·5 g.) with 6 c.c. of methyl alcohol (saturated with dry ammonia at 0°) at room temperature, short, prismatic crystals began to separate after 15 hours; 0·10 g. was collected after 18 hours, and a total of 0·26 g. after 4 days (yield 59%. In other experiments, the yield varied between 50 and 60%). The solution became light

brown, but there was no sign of the very characteristic series of colour changes which accompanied the formation of the corresponding amide from methyl xylotrimethoxyglutarate (Hirst and Purves, *loc. cit.*). The compound obtained behaved as an acid amide and liberated ammonia when heated above its melting point, giving a volatile, crystalline substance which was probably the imide. No change of colour was observed when the amide was heated in air (compare xylotrimethoxyglutardiamide). It was very slightly soluble in cold ether and in cold methyl alcohol, and could conveniently be recrystallised from the latter; it showed a considerably greater solubility in cold water : m. p. 232—233°, $[\alpha]_D + 50.0°$ in water ($c = 0.701$) (Found : $C = 43.7$; $H = 7.34$; $OMe = 41.1$; $N = 13.08$. $C_8H_{16}O_5N_2$ requires $C = 43.6$; $H = 7.27$; $N = 12.73$; $OMe = 42.3\%$). A parallel to the higher specific rotation of the amide as compared with that of the ester is to be found in the dimethyl ester and the diamide of dimethoxysuccinic acid (Purdie and Irvine, J., 1901, **79**, 960).

Methylation of Arabotrihydroxyglutaric Acid.—The acid was prepared by Kiliani's method (*Ber.*, 1888, **21**, 3007), except that after the oxidation with nitric acid and treatment with excess of calcium carbonate the calcium trihydroxyglutarate was precipitated from the cold filtrate by the addition of a small quantity of alcohol. The yellow, amorphous mass thus obtained was washed with a little water and dried on porous tile at 40°. The salt contained $1H_2O$, whereas Kiliani's product contained $3H_2O$. The substance showed the solubilities and properties of calcium trihydroxyglutarate described by previous workers (Found : $H_2O = 7.57$; $Ca = 18.35$ for the anhydrous substance. Calc. for $CaC_5H_6O_7,H_2O$, $H_2O = 7.63$, and for $CaC_5H_6O_7$, $Ca = 18.35\%$). Its identity was confirmed by determining the specific rotation of the free acid corresponding to the calcium salt, which was accomplished by measuring the rotation of the salt when dissolved in a slight excess of hydrochloric acid : $[\alpha]_D = -21.2°$ in water for $c = 1.065$ (as acid). The value quoted by Fischer (*Ber.*, 1891, **24**, 1844) is $-22.7°$.

The free acid (7 g.), prepared by treating the calcium salt with the calculated quantity of oxalic acid and evaporating the filtered solution in a vacuum, was methylated in methyl alcohol in the usual manner with methyl iodide and silver oxide, external cooling being necessary at first. The product was isolated, dissolved in methyl iodide, and subjected to two further treatments with methyl iodide and silver oxide to complete the methylation. On distilling the product (4.5 g.) from the third methylation, fractions were obtained : I, 1.95 g., b. p. 135°/15 mm., $n_D^{20°}$ 1.4353, $n_D^{12°}$ 1.4400;

II, 0·7 g., b. p. 140°/15 mm., $n_D^{18°}$ 1·4373. The former contained methyl oxalate (proved by the formation of oxamide on treatment with methyl-alcoholic ammonia), and a portion of this was redistilled, when 1·2 g. gave 0·7 g., b. p. 135°/12 mm., $n_D^{15°}$ 1·4370. This product was added to that forming the second portion of the first distillation and the material was identical with the ester previously identified as methyl trimethoxyglutarate, $[\alpha]_D + 45 \cdot 5°$ in methyl alcohol ($c = 1 \cdot 230$) (Found : C = 47·7; H = 7·28; OMe = 59·4; CO_2Me = 47·8%). Additional proof of identity was given by the isolation in good yield (0·6 g. gave 0·3 g.) of arabotrimethoxy-glutardiamide : m. p. 232°, alone or mixed with an authentic specimen, $[\alpha]_D + 49 \cdot 7°$ ($c = 1 \cdot 150$ in water); OMe = 41·3%. No trace of dimethoxysuccinamide could be detected, evidence being thus provided that the calcium salt used as starting material in this series of experiments was not contaminated with calcium tartrate.

Control Experiments.—The arguments by which the structure of trimethyl arabinose was deduced would be invalid in the event of there being any possibility for methylation of free hydroxy-groups to take place at some stage during the course of the experiments. In order to prove that no such methylation takes place under the conditions described above, experiments were carried out on the preparation of dimethyl tartrate under conditions chosen to conform as exactly as possible to those under which the oxidation product obtained from methylated arabinose was esterified. The ester (isolated in good yield) was the normal dimethyl tartrate (Found : OMe = 32·8%). Treatment of dimethyl tartrate with excess of boiling methyl alcohol containing 8% of nitric acid followed by neutralisation of the acid in boiling solution with freshly-prepared silver oxide gave unchanged dimethyl tartrate (Found : OMe = 34·7%). There is therefore no possibility for alkylation to take place under the very much milder conditions of the experiments described earlier in this paper.

LVII.—*Synthesis of Derivatives of γ-Arabinose.*

By STANLEY BAKER and WALTER NORMAN HAWORTH.

THE derivatives of *l*-arabinose which have hitherto been prepared are dextrorotatory, as indeed is the pentose itself. The authors have now isolated a series of lævorotatory compounds, which, although configurationally identical with those already known (Fischer, *Ber.*, 1895, **28**, 1156; Purdie and Rose, J., 1906, **89**, 1204), belong to the new group of γ-sugars and have a different oxide-ring structure.

The synthesis of these derivatives of γ-arabinose has been achieved by the initial condensation of *l*-arabinose with methyl-alcoholic hydrogen chloride at 18°, instead of conducting the reaction at 100° as prescribed by the previous authors. The new compound, *γ-methylarabinoside* (I), is characterised by its existence as a liquid having $[\alpha]_D - 71·3°$ in methyl alcohol, by its remarkable instability in presence of permanganate, and by the great ease with which it undergoes hydrolysis with acids of extreme dilution. Fischer's compound differs markedly in each of these respects and is strongly dextrorotatory. On methylation this distinction is maintained, for the new γ-methylarabinoside is converted into a mixture of the α- and β-forms of *trimethyl γ-methylarabinoside* (II), which again is lævorotatory ($- 55·8°$, in water). The β-form appears to be capable of selective hydrolysis with 0·036% hydrochloric acid, leaving the α-modification largely unchanged, but both are readily hydrolysed with 0·25% acid to *trimethyl γ-arabinose* (III), a liquid, $[\alpha]_D - 39·5°$ in water, exhibiting in a marked degree instability towards neutral permanganate. In all these respects, this methylated sugar contrasts strongly with the normal trimethyl arabinose investigated by Purdie and Rose (*loc. cit.*), and again by Hirst and Robertson (preceding paper), who have shown that the normal form is capable of hydrolysis only with 5% hydrochloric acid and has a rotation of $+ 127·2°$.

A determination of the structure of this trimethyl γ-arabinose discloses the reason for these differences in properties. Oxidation with nitric acid gives rise to a lactone of a trimethoxyhydroxy-valeric acid (IV), and also to a dimethoxyhydroxyglutaric acid (V). The latter product represents a further stage of oxidation than the former, inasmuch as the terminal group of the monobasic acid has undergone conversion into an acid group, giving a dibasic acid as the product, this secondary reaction being accompanied, however, by the elimination of one methoxyl residue.

That the secondary product of the oxidation is the acid (V) is

proved by its conversion into the completely methylated ester, dimethyl trimethoxyglutarate (VII), which forms a crystalline acid amide with ammonia. The structure allocated to both these oxidation products is supported by the following considerations. The trimethoxyvalerolactone (IV) is lævorotatory, more so, apparently, than the acid to which it gives rise on keeping in aqueous solution. Adopting Hudson's rule, the oxide ring must be situated on the left of the carbon chain and therefore it can only be a 1 : 3- or a 1 : 4- oxide. The possibility of the existence of the 1 : 5-oxide structure is eliminated, since the terminal group 5 remains intact as a methylated carbinol group, which, in the case of the secondary oxidation product, is seen to undergo further oxidation by loss of methoxyl to the corresponding dimethoxyhydroxyglutaric acid (V).

$$
\begin{array}{cccc}
\text{CH·OMe} & \text{CH·OMe} & \text{CH·OH} & \text{CO} \\
\text{HC·OH} & \text{HC·OMe} & \text{HC·OMe} & \text{HC·OMe} \\
O\;\;\text{HO·CH} \rightarrow & O\;\;\text{MeO·CH} \rightarrow & O\;\;\text{MeO·CH} \rightarrow & O\;\;\text{MeO·CH} \\
\text{CH} & \text{CH} & \text{CH} & \text{CH} \\
\text{CH}_2\text{·OH} & \text{CH}_2\text{·OMe} & \text{CH}_2\text{·OMe} & \text{CH}_2\text{·OMe} \\
\text{(I.)} & \text{(II.)} & \text{(III.)} & \text{(IV.)}
\end{array}
$$

$$
\begin{array}{ccc}
\text{CO}_2\text{H} & \text{CO}_2\text{Me} & \text{CO}_2\text{Me} \\
\text{CH·OMe} & \text{CH·OMe} & \text{CH·OMe} \\
\rightarrow\;\;\text{CH·OMe} \rightarrow & \text{CH·OMe} \rightarrow & \text{CH·OMe} \\
\text{CH·OH} & \text{CH·OH} & \text{CH·OMe} \\
\text{CO}_2\text{H} & \text{CO}_2\text{Me} & \text{CO}_2\text{Me} \\
\text{(V.)} & \text{(VI.)} & \text{(VII.)}
\end{array}
$$
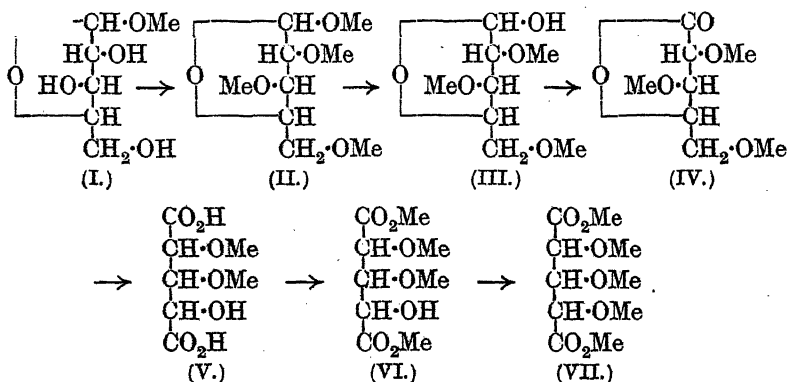
The choice between a 1 : 3- or propylene-oxide ring and that of a 1 : 4- or butylene-oxide structure for the trimethyl γ-arabinose is determined by the consideration that the existence of a propylene-oxide sugar has not hitherto been substantiated, whilst the 1:4-oxides are commonly known. A propylene-oxide structure has been ascribed to trimethyl and tetramethyl γ-glucose by Irvine and Patterson (J., 1923, **123**, 898; compare Irvine, J., 1922, **121**, 2146). A reference to the tetramethyl gluconolactone derived from the latter sugar on oxidation shows, however, that this lactone is dextrorotatory to a greater degree than the acid into which it is partly converted in water. The oxide ring of the latter should therefore be on the right of the carbon chain, and on this reasoning tetramethyl γ-glucose must be either a 1 : 4- or a 1 : 5-oxide. A 1 : 3- or propylene-oxide ring would, in the configuration of d-glucose, be situated on the left, and its lactone would thus be lævorotatory. If it be assumed that normal glucose is butylene-oxidic, then the most probable formula for tetramethyl γ-glucose is one having an

amylene-oxide structure (VIII) on the analogy of γ-fructose, and it follows that glucose diacetone, which is a γ-derivative, should be given the formula (IX).
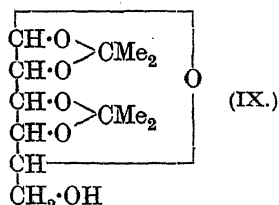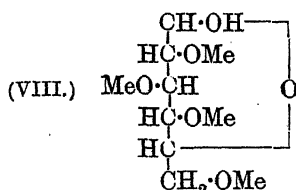
The accompanying paper by Hirst and Robertson furnishes an interesting corollary to the present investigation. These authors have demonstrated that the normal forms of *l*-arabinose and its derivatives are 1 : 5- or amylene-oxides, a conclusion which applies also to normal xylose. It thus appears that in the pentose series the γ-sugars belong to the butylene-oxide type on the analogy of galactose (Haworth, Ruell, and Westgarth, J., 1924, **125**. 2468).

<div align="center">EXPERIMENTAL.</div>

γ-Methylarabinoside.—Finely sieved, dried *l*-arabinose (10 g.) was shaken for 17 hours at room temperature in 200 c.c. of dried methyl alcohol (acetone-free), containing 2 g. of hydrogen chloride. Solution of the solid occurred after 6 hours, when the original specific rotation of arabinose (+ 107°) had diminished to − 1·0°; after 17 and 21 hours, a minimum value, $[\alpha]_D$ − 42·0°, was attained. After neutralisation with silver carbonate, followed by removal of solvent, the viscid product was repeatedly extracted with ethyl-acetate so long as the extracts showed a pronounced lævorotation. The combined extracts yielded a clear syrup (8 g.), which gave only a faint reaction with Fehling's solution before distillation : b. p. 173—175°/0·15 mm., $n_D = 1·4880$ (Found : C = 43·6; H = 7·4; OMe = 17·4. $C_6H_{12}O_5$ requires C = 43·9; H = 7·3; OMe = 18·9%). The maximum lævorotation recorded for the specimens was $[\alpha]_D$ − 71·3° (c = 0·8) in methyl alcohol, changing after 6 months to − 51·9°, whilst the value in water was − 46·8°. The γ-methylarabinoside instantaneously decolorised neutral permanganate.

Trimethyl γ-Methylarabinoside. — The undistilled γ-methyl-arabinoside (20 g.), showing $[\alpha]_D$ − 51·5° and prepared from 25 g. of *l*-arabinose, was methylated with methyl sulphate and sodium hydroxide followed by Purdie's reagents. The product, 17·5 g., was a colourless liquid, b. p. 85—87°/0·3 mm., $n_D = 1·4355$, $[\alpha]_D$ − 55·8° in water (c = 1·04) (Found : C = 52·3; H = 8·9;

OMe = 58·0. $C_9H_{18}O_5$ requires   C = 52·4;   H = 8·7;   OMe = 60·2%).   The compound decolorised neutral permanganate rapidly.

Trimethyl γ-Arabinose.—The β-form of the above γ-arabinoside was hydrolysed by digestion at 100° with N/100-hydrochloric acid; and during 3 hours the value of $[\alpha]_D$ changed from − 38·6° to − 58° and then remained constant.   At this stage, the solution actively reduced Fehling's solution.   The α-form required a higher concentration of acid to promote its hydrolysis, and by increasing the acid content to N/10 the specific rotation changed from − 58° to a constant value of − 32·2° during 3½ to 4 hours.

The mixture of α- and β-isomerides of trimethyl γ-methylarabinoside was completely hydrolysed by N/15-hydrochloric acid at 100° after 3½ to 4 hours, the rotation values recorded being :

Time in minutes ...	0	45	60	150	240
$[\alpha]_D$	−37·5°	−51·8°	−51·8°	−31·6°	−31·6°

The initial depression in the lævorotatory direction is followed by a rise to rotation values corresponding with those of the preceding experiments, and the form of the curve connecting these data is of the usual type.

The product of hydrolysis, trimethyl γ-arabinose, was isolated in the usual way, and distilled as a colourless liquid, b. p. 97—99°/ 0·18 mm., n_D = 1·4503 (Found : C = 49·9; H = 8·4; OMe = 49·3. $C_8H_{16}O_5$ requires C = 50·0; H = 8·3; OMe = 48·4%).   The sugar showed, in water, $[\alpha]_D$ = − 39·5°, and reduced Fehling's solution and neutral permanganate instantaneously.

Oxidation.—A solution of trimethyl γ-arabinose (5 g.) in 100 c.c. of dilute nitric acid (d 1·20) was heated at 90° until oxidation commenced, and then maintained at 75° for 19 hours, or until the evolution of nitrous fumes had ceased.   The solution was diluted with water, and the whole of the nitric acid distilled under diminished pressure at 40°, water being frequently added during this operation.   The residual syrup was dried by distilling from it methyl alcohol several times, and was finally esterified by methyl-alcoholic hydrogen chloride (3·0%).   Thereafter the solution was neutralised by barium carbonate, the use of silver carbonate being avoided for the reason that any free hydroxyl group might undergo methylation in the presence of methyl chloride (compare the methylation of malic acid, which occurs during ester formation by the action of methyl-iodide on silver malate).

The esterified product was a syrupy liquid (4·2 g.) which distilled completely at 105—118°/0·02 mm., and showed refractive indices varying from 1·4388 to 1·4437.   These data, along with the analytical figures, pointed to the non-homogeneity of the product,

and this conclusion was confirmed by subsequent experiments designed to separate the individual constituents.

The esterified oxidation product was hydrolysed by heating at 90° with 2·0% hydrochloric acid for 2 hours. The mineral acid was neutralised, using Congo-red as indicator, the solution evaporated under diminished pressure, and the residue extracted from mineral matter and distilled: b. p. 90°/0·03 mm., $n_D = 1·4430$. This distillate represented 75% of the oxidation product (leaving an undistilled residue which was subsequently examined), and immediately set to a hard mass of crystals; m. p. 29° (after draining on tile); $[\alpha]_D = -43·2°$ in water (changing to $-33·8°$ after 2 days, and to $-23·9°$ after 20 days) (Found: C = 50·5; H = 7·4; OMe = 46·0. Calc. for $C_8H_{14}O_5$, C = 50·5; H = 7·4; OMe = 48·9%). On titration, the compound behaved as a trimethoxy-valerolactone; 0·0906 required, on heating, 4·87 c.c. of $N/10$-sodium hydroxide. Calc. for $C_8H_{14}O_5$, 4·8 c.c.

The undistilled residue (25% of the total product) was a mixture of dimethoxyhydroxyglutaric acid and its lactone (Found: C = 42·37; H = 5·7. Calc. for $C_7H_{12}O_7$, C = 40·4; H = 5·8. Calc. for $C_7H_{10}O_6$, C = 44·2; H = 5·3%). After esterification with methyl alcohol, the product contained OMe = 53·6%, and after methylation with methyl iodide and silver oxide it gave the following analytical results: C = 47·9; H = 7·1; OMe = 60·0. Calc. for $C_{10}H_{18}O_7$, C = 48·0; H = 7·2; OMe = 62·0%. This specimen of dimethyl trimethoxyglutarate was dissolved in methyl alcohol which had been saturated with ammonia at 0°, and the corresponding amide, m. p. 223°, was isolated. The amide, the amount of which was small, was not recrystallised. In admixture with a specimen of the diamide of trimethoxyglutaric acid provided by Hirst and Robertson (loc. cit.) it melted at 225—227°.

LVIII.—*Phenyl Benzyl Diketone and some Derivatives.*

By THOMAS MALKIN and ROBERT ROBINSON.

THAT the methylene group in α-alkyloxy-ketones of the type of ω-methoxyacetophenone is characterised by considerable reactivity is clear from the use which has been made of these substances in

the synthesis of the anthocyanidins, and the work now to be described was instituted with the object of taking further advantage of this property. An experiment (p. 377) in which ω-methoxy-acetophenone and phenyl propyl ketone were put in competition for salicylaldehyde in boiling methyl-alcoholic potassium hydroxide solution showed that the former ketone exhibited the greater reactivity. The effect of the oxygen of the methoxyl group is doubtless to produce a general drift of electrons in the molecule towards it and this facilitates the acquirement of a negative charge by the carbon atom of the methylene group in the activated phase which determines the occurrence of the reaction. In the accompanying scheme the curved arrows show the covalency changes

$$\text{—C}{=}\text{CH—OMe}$$
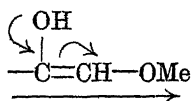
during activation of the enolic form of the ketone, and the straight arrow represents the general drift due to the oxygen of the methoxy-group. Here the effects are in the same direction and result in enhanced reactivity, whilst in phenyl propyl ketone the hydrogen atoms produce an electron drift in the opposite sense, and the reactivity due to the particular conjugation represented is diminished. Very numerous applications of this conception of the interaction of the electronic changes due to conjugation and the general polar or electrostatic induction effect can be made and one example in connexion with orientation is the explanation afforded of the frequent occurrence of substitution in the position situated between an o-p-directive group and a m-directive group, themselves in the m-position to one another. A case in point is the application of the Skraup reaction to m-nitroaniline. The two possible activations by conjugation are shown in (A) and (B), and the latter is assisted by the general electron drift due to the nitroxyl. The chief product
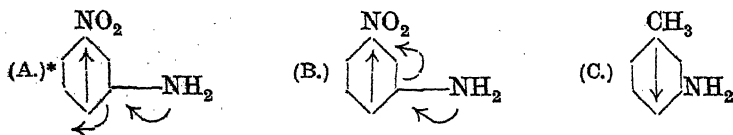
of the reaction is, in fact, 5-nitroquinoline. When the nitro-group is replaced by methyl, the direction of the general drift will be

* The curved arrows in (A) and (B) imply that free electrons of the N atom become covalency electrons of N and C_α in the nucleus and that C_α, in order to preserve its total covalency unaltered, abandons correspondingly $C_\alpha - C_\beta$ covalency electrons to the sole use of C_β.

reversed (C) and accordingly m-toluidine is converted in the Skraup reaction into 7-methylquinoline.

We have investigated some of the transformations of the arylidene-ω-methoxyacetophenones.

Phenyl β-methoxystyryl ketone, PhCO·C(OMe):CHPh, forms a colourless, crystalline dibromide the stability of which, although not of a high order, was unexpected. The failure of the group Ph·CO·C(OMe)Br to lose methyl bromide spontaneously is no doubt related to the unusual stability of the hydrate Ph·CO·CH(OH)$_2$. By reduction with hydrogen in presence of palladium, the unsaturated ketone is changed to a tetrahydro-derivative,

$$Ph·CH(OH)·CH(OMe)·CH_2Ph.$$

When subjected to somewhat vigorous hydrolysis by acids, the arylidene-ω-methoxyacetophenones yield α-diketones isomeric with the diaroylmethanes. Thus phenyl β-methoxystyryl ketone is changed by means of a hot solution of sulphuric acid in acetic acid into phenyl benzyl diketone, Ph·CO·CO·CH$_2$Ph, a substance which can be readily prepared in this manner. Whilst our work was proceeding, Dufraisse and Moureu placed on record a description of the compound, which was obtained by a different process (*Compt. rend.*, 1924, **178**, 6, 573). The diketone is almost certainly a tautomeric substance; it is yellow, oxidisable, soluble in aqueous sodium hydroxide, and gives a ferric chloride reaction. The facile condensation with o-phenylenediamine leads to phenylbenzyl-quinoxaline.

The most characteristic property of this diketone is, however, the remarkable ease with which it undergoes the benzil–benzilic acid type of transformation. It is rapidly converted by hot dilute aqueous sodium hydroxide into sodium α-benzylmandelate. This rearrangement could be represented as due to the migration of either the phenyl or the benzyl group, but, as it occurs more smoothly than in the case of benzil itself, the latter assumption seems the more natural :

$$Ph·CO·CO·CH_2Ph + H_2O \longrightarrow Ph·C(OH)(CO_2H)·CH_2Ph.$$
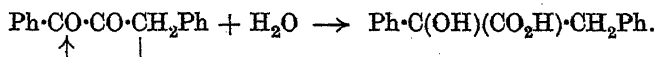
This interpretation is in harmony with the conclusions which Tiffeneau and Orékhov (compare *Annual Reports*, 1923, 115) have drawn from their experiments on intramolecular rearrangements of the pinacol–pinacolin type and also with the results of Claisen (*Z. angew. Chem.*, 1923, **36**, 478) on the alkylation of the phenols. In these and other cases, the high aptitude for migration possessed by the benzyl group has been emphasised. Corresponding unsaturated ketones, α-diketones, and their transformation products have been obtained in three other series.

EXPERIMENTAL.

Methoxyacetonitrile.—This intermediate in the preparation of some ω-methoxyacetophenones (Slater and Stephen, J., 1920, **117**, 314; Pratt and Robinson, J., 1923, **123**, 748) is best obtained by the following modification of Polstorff and Meyer's method (*Ber.*, 1912, **45**, 1911). Aqueous formaldehyde solution (reputed 40%, 35 c.c.) is gradually added with cooling in ice-water to sodium cyanide (19 g.), dissolved in water (38 c.c.). Powdered sodium cyanide (19 g.) is then introduced and when solution is complete a further quantity of aqueous formaldehyde (35 c.c.) is added with careful cooling. The mixture is kept at a low temperature for ½ hour and the thick, oily liquid or soft paste is then treated with methyl sulphate (80 c.c.), which is added in portions of 10 to 15 c.c. The mixture is thoroughly shaken, and not cooled until the temperature rises to 35°. After cooling for a few minutes in ice-water, the mixture is again allowed to warm to 35°; then it is cooled, and the next portion of methyl sulphate is added only when there is no further heat of reaction. The product is taken up in ether, and the separated extract dried with sodium sulphate and distilled. After separation from methyl sulphate by a preliminary fractionation under slightly reduced pressure, 39 g. (yield 70%), b. p. 119—120°, distilled at the ordinary pressure.

Phenyl β-Methoxystyryl Ketone, PhCO·C(OMe):CHPh.—Aqueous sodium hydroxide (20%) (5 c.c.) was added to a solution of ω-methoxyacetophenone (5 g.) and benzaldehyde (3·5 g.) in ethyl alcohol (30 c.c.). After 12 hours, the greater part of the alcohol was distilled from the steam-bath, and the residue diluted with water and extracted with ether. The ethereal solution was dried over sodium sulphate and distilled under diminished pressure; 2·4 g. of a mixture of benzaldehyde and ω-methoxyacetophenone were recovered and 4·8 g. of a pale yellow oil, b. p. 202—204°/13 mm., which solidified on cooling, were obtained. The substance is readily soluble in most organic solvents, but may be crystallised by cooling a saturated solution in ethyl alcohol or light petroleum to 0°. The rectangular plates, m. p. 35°, are almost colourless (Found : C = 80·9; H = 5·8. $C_{16}H_{14}O_2$ requires C = 80·7; H = 5·9%). The citron-yellow solution in sulphuric acid becomes yellowish-green and finally deep violet on heating.

Phenyl αβ-Dibromo-α-methoxy-β-phenylethyl Ketone,

PhCO·CBr(OMe)·CHBrPh.
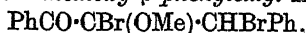
—Phenyl β-methoxystyryl ketone (6 g.), dissolved in ether (10 c.c.), was gradually treated at 0° with bromine (4 g.). The *dibromide* (4·7 g.) crystallised in a few minutes, and a further quantity

(4—5 g.) of somewhat less pure product was obtained on evaporation of the solution. The substance crystallises from benzene in colourless needles, m. p. 103° (Found : C = 48·5; H = 3·6. $C_{16}H_{14}O_2Br_2$ requires C = 48·2; H = 3·5%). In the course of a few days red specks appear in the crystals, but attempts to obtain definite products of decomposition have not yet been successful. This is probably due to the circumstance that the substance tends to lose the elements of methyl bromide as well as of hydrogen bromide.

It was shown by titration that, when boiled with water, the dibromide yields a molecular proportion of hydrogen bromide, but the resulting yellow oil could not be satisfactorily purified. A Zeisel determination (Found : MeO = 5·5. $C_{15}H_{10}OBr\cdot OMe$ requires MeO = 9·8%) showed that hydrolysis at the methoxyl group must occur to some extent. Boiling aqueous sodium hydroxide attacks the dibromide with formation of sodium bromide (2 mols.). The final ethereal mother-liquor from the preparation deposited yellow crystals, m. p. 59°, but the quantity obtained was insufficient for further investigation.

Phenyl Benzyl Diketone.—A solution of phenyl β-methoxystyryl ketone (2 g.) in acetic acid (9 c.c.) and concentrated sulphuric acid (1 c.c.) was heated over a free flame until the yellow solution became deep brownish-red. Prolonged heating is disadvantageous and the time necessary to bring the liquid to the boiling point usually suffices. After dilution with water and extraction with ether, the ethereal layer was washed with water and then with successive small portions of 10% aqueous sodium hydroxide. These deep orange, alkaline washings were expeditiously acidified with hydrochloric acid in presence of ice, and the diketone was again taken up in ether. The extract was dried over sodium sulphate, the greater part of the solvent removed by distillation, and the remainder by evaporation in a vacuum, leaving 1·7 g. of a yellow, crystalline solid. The substance crystallises from methyl alcohol or ether in pale yellow prisms, m. p. 65° (Dufraisse and Moureu, *loc. cit.*, 67—68°) (Found : C = 80·6; H = 5·7. Calc., C = 80·4; H = 5·4%). This diketone is readily soluble in most organic solvents; the crystals rapidly become oily on exposure. In alcoholic solution, a purplish-brown coloration is developed on the addition of ferric chloride.

2-Phenyl-3-benzylquinoxaline.—A solution of phenyl benzyl diketone (1·2 g.) and *o*-phenylenediamine (0·6 g.) in ethyl alcohol (3 c.c.) was gently heated on the steam-bath for 20 minutes. The compact, yellow crystals (0·7 g.) that separated on cooling crystallised from ethyl alcohol in almost colourless, lustrous needles,

m. p. 97° (Found : C = 83·1; H = 5·7; N = 9·6. $C_{21}H_{16}N_2$ requires C = 83·1; H = 5·4; N = 9·5%). The orange solution in concentrated sulphuric acid becomes colourless on dilution with water.

Phenyl β : 4-*Dimethoxystyryl Ketone*, Ph·CO·C(OMe)CH·C_6H_4·OMe. —Aqueous sodium hydroxide (5 c.c. of 20%) was added to a solution of ω-methoxyacetophenone (5 g.) and anisaldehyde (4·5 g.) in ethyl alcohol (30 c.c.). Next day, 3·5 g. of product had crystallised, and a further portion (1 g.) separated on cooling the solution in ice. The mother-liquor was treated as in the preparation of phenyl β-methoxystyryl ketone, and unchanged material (2·5 g.) and the unsaturated ketone (1 g.) were so obtained. The total yield was therefore 5·5 g. The substance crystallises from alcohol, in which it is moderately readily soluble, in hard, pale yellow, rectangular prisms, m. p. 75°, b. p. 238—242°/14 mm. (Found : C = 76·3; H = 5·8. $C_{17}H_{16}O_3$ requires C = 76·1; H = 6·0%). The orange solution in sulphuric acid becomes deep yellowish-brown on heating. Attempts to prepare a crystalline dibromide were unsuccessful.

Phenyl 4-*Methoxybenzyl Diketone*, Ph·CO·CO·CH_2·C_6H_4·OMe.— The hydrolysis of the foregoing substance by means of sulphuric acid in acetic acid solution gave unsatisfactory yields (30%), but the use of hydrobromic acid effected a considerable improvement. The anisylidene derivative (2 g.) was dissolved in acetic acid (10 c.c.), concentrated aqueous hydrobromic acid (4 c.c.) added, and the orange liquid heated over a free flame until there was a rather sudden change of colour to a dirty red. The remaining procedure followed exactly that described in the case of phenyl benzyl ketone and there resulted 1·7 g. of a yellow, crystalline mass. The substance is not very stable and crystallises best from methyl alcohol, separating in pale yellow, prismatic needles, m. p. 68° (Found : C = 75·2; H = 5·6. $C_{16}H_{14}O_3$ requires C = 75·6; H = 5·5%). In alcoholic solution, the substance gives a purplish-brown coloration with ferric chloride, and on condensation with *o*-phenylene-diamine in alcoholic solution it readily yields 2-*phenyl*-3-*p*-*methoxy-benzylquinoxaline*, which crystallises from ethyl alcohol in colourless needles, m. p. 119° (Found : C = 80·9; H = 5·7. $C_{22}H_{18}ON_2$ requires C = 81·0; H = 5·5%) and gives a brown solution in sulphuric acid.

When the alkaline solution of the diketone was agitated with methyl sulphate, phenyl β : 4-dimethoxystyryl ketone was regenerated in good yield. The crystallised substance, m. p. 75°, exhibited an unaltered melting point when mixed with an authentic specimen.

4-Methoxyphenyl β-Methoxystyryl Ketone,

$MeO \cdot C_6H_4 \cdot CO \cdot C(OMe)\text{:}CHPh.$

—This substance was prepared in the same way as phenyl β-methoxy-styryl ketone (above). ω : 4-Dimethoxyacetophenone (4 g.) and benzaldehyde (2·4 g.) yielded 3·3 g. of a yellow oil, b. p. 240—250°/33 mm., which crystallised, and 2 g. of recovered material, whilst the residue in the flask gave 0·5 g. of the condensation product by crystallisation from alcohol. The substance is readily soluble in most organic solvents and crystallises from ethyl alcohol in colourless, rectangular prisms, m. p. 74° (Found : C = 76·1; H = 6·0. $C_{17}H_{16}O_3$ requires C = 76·1; H = 6·0%). The deep yellow solution in sulphuric acid becomes intensely orange-red on warming and crimson on heating more strongly.

4-Methoxyphenyl benzyl diketone, $MeO \cdot C_6H_4 \cdot CO \cdot CO \cdot CH_2Ph$, obtained from the foregoing unsaturated ketone by the same method and in the same yield as described above in the case of an isomeride, crystallises from ether or alcohol in yellow plates, m. p. 82° (Found : C = 75·6; H = 5·7. $C_{16}H_{14}O_3$ requires C = 75·6; H = 5·5%). The properties of the substance closely resemble those of phenyl benzyl diketone. Condensation with *o*-phenylenediamine leads to 2-p-*methoxyphenyl*-3-*benzylquinoxaline*, which crystallises from alcohol in colourless, silky needles, m. p. 141° (Found : C = 80·8; H = 5·7. $C_{22}H_{18}ON_2$ requires C = 81·0; H = 5·5%). The solution in sulphuric acid is Bordeaux red.

4-Methoxyphenyl β : 4-Dimethoxystyryl Ketone,

$\qquad MeO \cdot C_6H_4 \cdot CO \cdot C(OMe)\text{:}CH \cdot C_6H_4 \cdot OMe.$

—The condensation of anisaldehyde and ω : 4-dimethoxyaceto-phenone was carried out in the manner prescribed for the preparation of phenyl β-methoxystyryl ketone, except that after the removal of unchanged materials by distillation under diminished pressure the residue was stirred with alcohol and so induced to crystallise. The substance crystallises from alcohol in faintly yellow, rectangular plates, m. p. 72·5° (Found : C = 72·5; H = 6·2. $C_{18}H_{18}O_4$ requires C = 72·5; H = 6·0%). The orange-red solution in sulphuric acid becomes rich crimson on heating. Comparison of the colour of the derivatives of benzylideneacetophenone now described shows that a methoxy-group in the *p*-position in the benzylidene nucleus has auxochromic character, whilst a similar substitution in the acetophenone nucleus has a feeble bathochromic influence.

On hydrolysis with hydrobromic acid in acetic acid solution, this trimethoxybenzylideneacetophenone yields *4-methoxyphenyl* 4-*meth-oxybenzyl diketone*, $MeO \cdot C_6H_4 \cdot CO \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot OMe$, in almost theoretical amount. This substance closely resembles phenyl

benzyl diketone and crystallises from ethyl alcohol in yellow prisms, m. p. 92° (Found : C = 71·7; H = 5·8. $C_{17}H_{16}O_4$ requires C = 71·8; H = 5·6%). 2-p-*Methoxyphenyl*-3-p-*methoxybenzylquin-oxaline* crystallises from alcohol in colourless, silky needles, m. p. 123° (Found : C = 77·5; H = 5·7. $C_{23}H_{20}O_2N_2$ requires C = 77·5; H = 5·6%). This base dissolves in concentrated hydrochloric acid to an orange-yellow solution, but the salt is dissociated on dilution with water. The solution in sulphuric acid is Bordeaux red. None of the quinoxalines now described exhibits fluorescence in acid or neutral solution.

α-*Benzylmandelic Acid and Derivatives.*—When solutions of phenyl benzyl diketone or its derivatives in aqueous sodium hydroxide of any convenient concentration are boiled, the deep orange colour rapidly fades to pale yellow and acidification of the cooled liquid with hydrochloric acid precipitates colourless crystals of the corresponding hydroxy-acid (yield nearly theoretical). These acids are sparingly soluble in hot water and very readily soluble in alcohol; they can best be crystallised from benzene.

α-*Benzylmandelic acid* occurs in colourless needles, m. p. 164° (Found : C = 74·7; H = 6·1. $C_{15}H_{14}O_3$ requires C = 74·4; H = 5·8%). The substance is oxidised by chromic acid in acetic acid solution with formation of benzil, whilst the action of bromine on a solution in aqueous sodium carbonate produces a neutral compound which contains bromine and crystallises from alcohol in colourless flakes, m. p. 54°. This is probably desyl bromide, m. p. 55°. On distillation under ordinary pressure, the acid (0·7 g.) yielded α-phenylcinnamic acid (0·5 g.), m. p. 170°, identified by the method of mixed melting point, and a small amount of stilbene, m. p. 124°.

The acid, $C_{15}H_{14}O_3$, m. p. 160—161°, which Bogdanowska (*Ber.*, 1892, **25**, 1276) obtained by the action of 1% aqueous potassium hydroxide on dibenzyl ketone is doubtless identical with α-benzyl-mandelic acid. It may be that dibenzyl ketone suffers auto-condensation followed by oxidation and production of phenyl benzyl diketone and in its turn benzylmandelic acid.

α-4-*Methoxybenzylmandelic acid*, OH·CPh(CO$_2$H)·CH$_2$·C$_6$H$_4$·OMe, crystallises from benzene in prismatic needles, m. p. 193° (Found : C = 70·7; H = 6·1. $C_{16}H_{16}O_4$ requires C = 70·6; H = 5·9%).

The isomeric 4-*methoxy-α-benzylmandelic acid*,
$$MeO·C_6H_4·C(OH)(CO_2H)·CH_2Ph,$$
crystallises in colourless needles, m. p. 181° (Found : C = 70·6; H = 6·1%).

4 : 4'-*Dimethoxy-α-benzylmandelic acid,*

$$\text{MeO·C}_6\text{H}_4\text{·C(OH)(CO}_2\text{H)·CH}_2\text{·C}_6\text{H}_4\text{·OMe,}$$
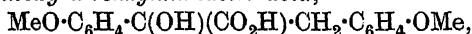
crystallises from benzene in colourless, prismatic needles, m. p. 170° (Found : C = 67·5; H = 6·1. $C_{17}H_{18}O_5$ requires C = 67·6; H = 6·0%).

α-*Hydroxy-β-methoxy-αγ-diphenylpropane,*

$$\text{Ph·CH(OH)·CH(OMe)·CH}_2\text{Ph.}$$
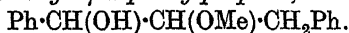
—The reduction of phenyl β-methoxystyryl ketone by means of hydrogen in presence of palladium in acetic acid solution was unsuccessful. The ketone (4·5 g.), dissolved in ethyl alcohol (100 c.c.), was reduced during 3·5 hours by agitation with hydrogen, 15 c.c. of a solution of palladous chloride (0·5%) and gum arabic (0·5%) having been added. Absorption of hydrogen was still occurring, so the process was continued for a further 2·5 hours, when absorption of gas ceased. The filtered solution was distilled to remove alcohol, and the oil remaining was isolated with the aid of ether and distilled, 3·5 g., b. p. 197°/15 mm., being obtained [Found : C = 79·1; H = 7·4; MeO = 11·9, 11·8 (first expt.), 12·6 (second expt.). $C_{16}H_{18}O_2$ requires C = 79·3; H = 7·4; MeO = 12·8%]. The readily soluble, colourless oil does not yield a semicarbazone. It dissolves in sulphuric acid to a crimson solution which, on gently heating, becomes nearly colourless with simultaneous deposition of a deep bluish-grey solid.

Relative Reactivity of ω-Methoxyacetophenone and Phenyl Propyl Ketone.—ω-Methoxyacetophenone (7·5 g.; 1 mol.), b. p. 115—116°/15 mm., phenyl propyl ketone (7·4 g.; 1 mol.), b. p. 118—120°/15 mm., salicylaldehyde (7·6 g.; 1·25 mols.), and potassium hydroxide (4 g.) were dissolved in methyl alcohol (100 c.c.), and the mixture boiled for 24 hours. The oil, insoluble in alkali, was then isolated by means of ether and distilled, 10·5 g., b. p. 115—122°, being obtained (Found : MeO = 5·2%), and from this result it may be calculated that the whole of the phenyl propyl ketone was recovered unchanged whilst about 5 g. of the ω-methoxyacetophenone had been converted into the salicylidene derivative.

LIX.—*The Additive Formation of Four-membered Rings. Part VI. The Addition of Azo-compounds to Ethylenes and some Transformations of the Dimethylene-1 : 2-di-imine Ring.*

By CHRISTOPHER KELK INGOLD and STANLEY DOUGLAS WEAVER.

THE experiments described in this paper were made with the object of ascertaining the tendency of the groups N=N and C=C to undergo additive union with each other to form a ring, and of increasing our knowledge of the somewhat obscure heterocyclic types which can be produced in this way.

The azo-group in azobenzene possesses a very small additive power, and this may be ascribed to the engagement by the phenyl groups of the residual affinity of the unsaturated residue : Ph—N=N—Ph. When, however, the phenyl groups are replaced by other groups such as carbethoxyl, which have a much smaller affinity demand, structures are produced, such as Ph—N=N—CO$_2$Et and CO$_2$Et—N=N—CO$_2$Et, possessing free residual affinity and hence greater additive power. These azo-esters were therefore chosen as representative compounds for the purpose of studying the additive reactions of the azo-group.

The ethylene derivatives were selected in accordance with the principle which emerged during the earlier parts of this research, that substitution, especially by a large *gem*-grouping like the *gem*-diphenyl group, favours the production of stable, four-membered rings. Styrene, *as*-diphenylethylene, and diphenylketen were the examples chosen.

Phenylazocarboxylic ester combines with great ease with diphenylketen, forming a four-membered ring-compound * (I). This compound, which belongs to a heterocyclic family very few members of which are at present known, undergoes a number of interesting changes.

$$\text{NPh}\dot{.}\text{N}\cdot\text{CO}_2\text{Et} + \text{CPh}_2\dot{.}\text{CO} \longrightarrow$$

$$\text{(I.)} \quad \begin{array}{l} \text{PhN—N}\cdot\text{CO}_2\text{Et} \\ \text{Ph}_2\text{C—C O} \end{array} \underset{\text{Ac}_2\text{O}}{\overset{\text{NaOH}}{\rightleftarrows}} \begin{array}{l} \text{PhN—NH}\cdot\text{CO}_2\text{Et} \\ \text{Ph}_2\text{C—CO}_2\text{H} \end{array} \text{(II.)}$$
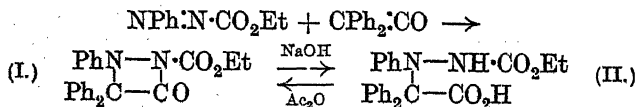
The action of hot aqueous-alcoholic sodium hydroxide leads to an acidic substance having an additional H$_2$O in its composition. On dehydrating this with acetic anhydride, the original substance

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* The direction of this addition conforms to the theory of alternate polarities, unlike many of the cases previously discussed (compare, for instance, Ingold and Weaver, J., 1924, **125**, 1456).

is regenerated. Since the constitution assigned to the original ·substance is analogous to that of a β-lactam, these reactions may legitimately be compared with those of the lactam (III), which, as Staudinger, Klever, and Köbner showed (*Annalen*, 1911, **374**, 13), is converted by potassium hydroxide into an acid (IV) from which the lactam can be regenerated by the agency of acetyl chloride :

$$(\text{III.}) \quad \begin{array}{l} \text{PhHC—N·CH}_2\text{Ph} \\ \text{Me}_2\text{C—CO} \end{array} \xrightleftharpoons[\text{AcCl}]{\text{KOH}} \begin{array}{l} \text{PhHC—NH·CH}_2\text{Ph} \\ \text{Me}_2\text{C—CO}_2\text{H} \end{array} \quad (\text{IV.})$$
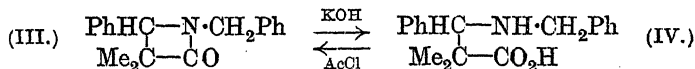
The closeness of the analogy leaves little doubt but that alkali opens the ring in (I) in the manner shown, and that formula (II) may be ascribed to the acid produced.

A remarkable ring-transformation takes place when compound (I) is boiled with mineral acids. The product of the reaction is isomeric with the original substance, but possesses very different properties. The key to the nature of this isomeric change is given by the fact that, whereas the original four-membered ring compound does not, of course, form an acetyl derivative, its transformation product is readily acetylated, giving a monoacetyl compound; this can be explained only on the assumption that a hydrogen atom has passed from one of the phenyl groups to nitrogen. Formula (I) represents a ditertiary hydrazine, $R^IR^{II}N·NR^{III}R^{IV}$, in which two of the groups, such as R^{II} and R^{III}, together participate in a ring. Now the ditertiary hydrazines are known to be especially addicted to transformations of the ortho-semidine type. Thus tetraphenylhydrazine (V), although its constitution admits of any of the four rearrangements to which aromatic hydrazines are liable (the ortho- and para-semidine, and the ortho- and para-benzidine changes), actually isomerises exclusively to the base (VI) (Wieland, *Annalen*, 1911, **381**, 200) :
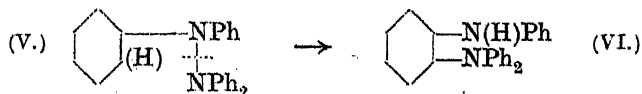
The structure of the cyclic hydrazine (I) admits of an ortho- or para-semidine change, but not a benzidine change, since only one of the nitrogen atoms carries a phenyl group. On the grounds of analogy, therefore, it is highly probable that the observed transformation is of the ortho-semidine type, and may be formulated as in the preceding case :
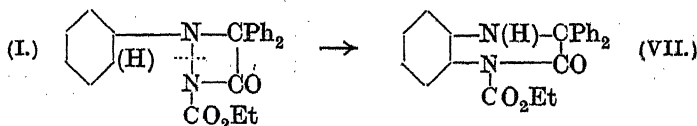
and this probability amounts to a practical certainty when it is reflected that the only possible alternative, a para-semidine rearrangement, is, in this case, intrinsically unlikely, since the product would have formula (VIII), which is quite out of keeping with its ease of formation and stability. Formula (VII), on the other hand, is in complete harmony with the properties of the substance.
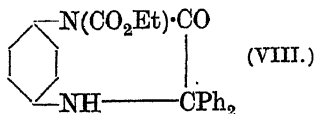
One other transformation is of sufficient interest to be mentioned here. The compound (VII) does not react in the cold with phosphorus pentachloride, but if heated with this reagent it loses ethyl chloride, giving an acid chloride (IX), which, by the inter-action of its acyl chloride residue with the basic imino-group, yields the tricyclic compound (X):
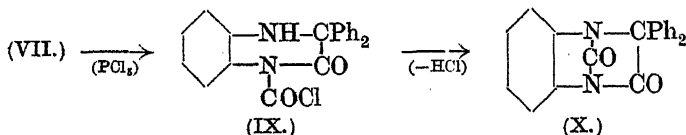
This substance belongs to the type represented by the formula $N{<}{\overset{a}{\underset{b}{}}}{>}N$ (XI), where a, b, and c denote three different groups,

one of these (at least) being unsymmetrical with respect to the two nitrogen atoms. The space model of (X) lies in three planes (like that of camphor), and the compound should therefore be capable of optical activity depending on the asymmetry of its two tervalent nitrogen atoms (Moore, P., 1914, 182). Moore and Doubleday (J., 1921, **119**, 1170) recently prepared some asymmetric, tervalent nitrogen compounds of a similar type, but these contained methylene groups in place of the carbonyl groups in (X) and exhibited certain changes of colour and molecular weight in solution. It was hoped that the introduction of the cyclic -CO—N— linking in place of the -CH$_2$—N- linking might confer greater stability, and the opportunity of completing the synthesis of a stable substance of type (XI) was therefore followed up in the manner described. The compound (X) is, in fact, remarkably stable and is colourless in the solid state and in solution. No special proof is offered here regarding its constitution, but the method of formation appears to place this beyond any reasonable doubt.

Amongst the additive ring syntheses an account of which will be found in the experimental portion are the addition reactions between styrene and *as*-diphenylethylene on the one hand and azodicarboxylic ester on the other. The products belong to an almost unknown family of six-membered rings, the hexahydro-*v*-tetrazines, which, to judge by the examples described (XII and XIII), possess unexpected stability.

$$
\text{(XII.)} \quad
\begin{array}{c}
\text{N·CO}_2\text{Et} \\
\text{PhHC} \diagup \diagdown \text{N·CO}_2\text{Et} \\
\text{H}_2\text{C} \diagdown \diagup \text{N·CO}_2\text{Et} \\
\text{N·CO}_2\text{Et}
\end{array}
\qquad
\begin{array}{c}
\text{N·CO}_2\text{Et} \\
\text{Ph}_2\text{C} \diagup \diagdown \text{N·CO}_2\text{Et} \\
\text{H}_2\text{C} \diagdown \diagup \text{N·CO}_2\text{Et} \\
\text{N·CO}_2\text{Et}
\end{array}
\quad \text{(XIII.)}
$$
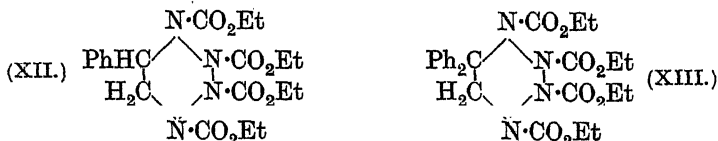
EXPERIMENTAL.

Ethyl azodicarboxylate was prepared by a modification of Diels's method (*Ber.*, 1911, **44**, 3020). Hydrazine sulphate (130 g.) was dissolved in a minimum of water, and the base liberated by potassium hydroxide (112 g. in a little water). The precipitation of potassium sulphate was furthered by adding alcohol, and the filtered solution treated with a mixture of 70 c.c. of ethyl chloroformate and 200 c.c. of ethyl alcohol. After heating for one hour on the water-bath, the precipitated hydrazine hydrochloride was collected, the filtrate evaporated at the ordinary temperature, and the product crystallised from boiling water. The hydrazo-ester (m. p. 131°; yield almost theoretical) was dissolved in concentrated nitric acid (5 parts) contained in a separating funnel, and the mixture allowed to warm slightly (this occurs spontaneously with the formation of nitrogen peroxide, the liquid becoming green). When the mixture became turbid and an oil separated on the surface, the lower layer was run off and cooled somewhat by a freezing mixture, whilst the oil, dissolved in ether, was washed once with water to prevent further oxidation by the excess of nitric acid contained in it. The acid layer was then replaced in the funnel, allowed to warm again, and the process repeated until no more oil could be obtained. The combined ethereal solutions were washed about 15 times with 10% sodium carbonate solution, then with water, dried over sodium sulphate, and the ether removed. The residual oil was purified by distillation and the ethyl azodicarboxylate collected at 121—125°/16 mm.

Ethyl hydrazotricarboxylate, $\text{CO}_2\text{Et·NH·N(CO}_2\text{Et})_2$, a by-product in the above preparation, was collected in the fraction, b. p. 199—203°/22 mm., which on re-distillation yielded a neutral, colourless oil, b. p. 200—201°/23 mm. (Found: $C = 42.95$; $H = 6.47$; $N = 11.3$; M in freezing benzene = 276, 258. $\text{C}_9\text{H}_{16}\text{O}_6\text{N}_2$ requires $C = 43.5$; $H = 6.4$; $N = 11.3\%$; $M = 248$).

Ethyl benzenazocarboxylate was prepared by a modified form of Heller and Widman's methods (*Annalen*, 1891, **263**, 287; *Ber.*, 1895, **28**, 1927). Ethyl chloroformate (50 g.) was added gradually and with vigorous stirring to an ice-cold solution of 100 g. of phenylhydrazine in 500 c.c. of dry ether. The red oil, which remained when the ether was evaporated from the filtered solution, was dissolved in benzene, and ligroin (b. p. 60—80°) added to bring about the separation of the hydrazo-ester in nearly colourless needles, m. p. 80—82° (yield 60%). Forty grams of this, dissolved in cold glacial acetic acid, were treated gradually with an aqueous solution of 12 g. of potassium permanganate. After the excess of the permanganate had been destroyed with hydrogen peroxide, the mixture was poured into water, and the oil extracted with ether and washed several times with sodium carbonate and then with water. The extract was dried with calcium chloride and evaporated, and the azo-ester freed from the last traces of ether by the passage of a current of dry air at 40° (yield 90%).

Addition of Ethyl Azodicarboxylate to Diphenylketen : Formation of Ethyl 3 : 5-*Diketo*-4 : 4 : 6 : 6-*tetraphenylhexahydropyridazine*-1 : 2-*dicarboxylate,* $\begin{matrix} \text{CPh}_2\cdot\text{N(CO}_2\text{Et)}\cdot\text{N(CO}_2\text{Et)} \\ \text{CO}\text{——}\text{CPh}_2\text{——}\text{CO} \end{matrix}$ *.—A light-petroleum solution containing ethyl azodicarboxylate (7·5 g.) and diphenylketen (8·6 g.) was kept for 24 hours out of contact with air and moisture. The crystals which had separated were recrystallised several times from ethyl alcohol, colourless needles, m. p. 129—131°, being obtained (Found: C = 72·61; H = 5·30; N = 5·03. $C_{34}H_{30}O_6N_2$ requires C = 72·44; H = 5·34; N = 4·98%). The compound gives no colour with ferric chloride and is stable to permanganate in the cold; it is, however, fairly sensitive to hydrolysing agents.

Hydrolytic Fission : Anhydro-α-diphenylacetyl-α(or β)-carboxy-β(or α)-carbethoxyhydrazine-β-diphenylacetic Acid, $\begin{matrix} \text{CPh}_2\text{—N}\cdot\text{N(CO}_2\text{Et)}\cdot\text{CO}\cdot\text{CHPh}_2 \\ \text{CO}\cdot\text{O}\cdot\text{CO} \end{matrix}$ or $\begin{matrix} \text{CPh}_2\cdot\text{N(CO}_2\text{Et)}\cdot\text{N}\cdot\text{CO}\cdot\text{CHPh}_2. \\ \text{CO}\text{——}\text{O}\text{——}\text{CO} \end{matrix}$ —The pyridazine (4 g.) was boiled with concentrated hydrochloric acid (15 c.c.) and alcohol (70 c.c.) until crystals began to separate. After cooling, the product was collected and crystallised from a mixture of alcohol and ethyl acetate, from which colourless needles separated, m. p. 155—156° (yield 3·4 g.) (Found: C = 71·57;
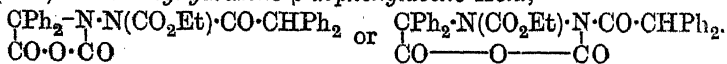
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* This γ-diketopyridazine formula is ascribed in preference to the δ-diketopyridazine formula, $\begin{matrix} \text{CO}\cdot\text{N(CO}_2\text{Et)}\cdot\text{N}\cdot\text{CO}_2\text{Et} \\ \text{CPh}_2\text{—CPh}_2\text{—CO} \end{matrix}$, owing to the close analogy with the γ-diketopiperidines of Staudinger, which, unlike the isomeric δ-diketopiperidines, are readily split by hydrolytic agents (compare *Annalen*, 1911, **374**, 11).

H = 5·19; N = 5·06. $C_{32}H_{28}O_6N_2$ requires C = 71·63; H = 5·22; N = 5·22%). The compound is stable towards permanganate and gives no colour with ferric chloride.

Addition of Ethyl Benzeneazocarboxylate to Diphenylketen : Formation of Ethyl 4-Keto-2 : 3 : 3-triphenyldimethylene-1 : 2-di-imine-1-carboxylate (I).—The azo-ester (5·1 g.) was added to a solution of 5·6 g. of the keten in 150 c.c. of light petroleum, and the mixture kept for 24 hours out of contact with air and moisture. The crystals were then collected, drained, and crystallised from ether, alcohol, dilute acetic acid, or chloroform–ligroin, from any of which colourless prisms separated, m. p. 132—133° (yield 70%) (Found : C = 74·30; H = 5·50; N = 7·61. $C_{23}H_{20}O_3N_2$ requires C = 74·20; H = 5·38; N = 7·53%). The compound gives no colour with alcoholic ferric chloride, and does not reduce permanganate in the cold; nor can it be reduced by zinc in boiling acetic acid. It yields no acetyl derivative, and is, for example, unchanged by prolonged boiling with acetic anhydride. On distillation under reduced pressure, an operation in which so many four-membered ring compounds are broken down into unsaturated substances ("thermal division"), this compound passes over unchanged. It is, however, sensitive to hot mineral acids and alkalis.

Ring Fission by Alkaline Hydrolysis : β-Phenyl-α-carbethoxyhydrazine-β-diphenylacetic Acid (II).—A solution of the ringcompound (3·4 g.) in 35 c.c. of alcohol was boiled with 10 c.c. of 10% aqueous sodium hydroxide for about 5 minutes, cooled, and acidified with hydrochloric acid. The precipitated oil was extracted with chloroform, and recovered by evaporation of the solvent after drying with calcium chloride. It readily solidified on rubbing with ether, and was then crystallised from chloroform–ligroin, from which slender, colourless needles, m. p. 157—158°, were obtained. Yield, 3·5 g. (Found : C = 70·38; H = 5·84; N = 7·16. $C_{23}H_{22}O_4N_2$ requires C = 70·76; H = 5·64; N = 7·18%). It is a weak acid, soluble in dilute sodium hydroxide solution, but only slowly soluble in sodium hydrogen carbonate.

Closure of the Ring by Dehydration with Acetic Anhydride.—The acid (0·3 g.) was boiled for about 3 minutes with 2 c.c. of acetic anhydride, and the product warmed with water to remove the excess of the latter. The oily precipitate was extracted with chloroform, and the extract washed with water, dried with calcium chloride, and evaporated. The residue, on rubbing with ether, solidified and was crystallised from alcohol, from which the ringcompound (I) separated (yield 0·25 g.). It was identified by m. p. (132—133°), and mixed m. p., and by analysis (Found : C = 73·7; H = 5·4%).

Conversion of a 4-Membered Ring into a 6-Membered Ring by o-Semidine Change : Ethyl 3-Keto-2 : 2-diphenyltetrahydroquinoxaline-4-carboxylate (VII).—A solution of 5 g. of the ring-compound (I) in 40 c.c. of alcohol was boiled with 20 c.c. of concentrated hydrochloric acid until crystallisation commenced. The solid product was collected from the cooled solution and crystallised from chloroform–ligroin, dilute alcohol, or dilute acetic acid, from any of which it separated in bunches of colourless needles, m. p. 165—166° (yield almost theoretical).

Although this product melted fairly sharply, close examination revealed the presence of about 10% of an impurity which could not be removed by fractional crystallisation. After many trials, the following process was adopted. The substance (3 g.) was dissolved in 15 c.c. of alcohol and boiled with 30 c.c. of 10% sodium hydroxide. The small quantity of solid which separated was collected after cooling (0·3 g.). After crystallisation from ligroin–chloroform it yielded slender, colourless needles, m. p. 180—181° (Found : C = 75·97; H = 5·12; N = 9·17. $C_{20}H_{16}O_2N_2$ requires C = 75·85; H = 5·06; N = 8·86%). This *substance* is, apparently, a ketotriphenyloxadiazole, but the quantity obtained was too small for investigation.

The mother-liquors from this substance deposited the quinoxaline, which could be washed with dilute acid and crystallised; but a more convenient process was to add hydrochloric acid and extract the oily precipitate with chloroform. The product recovered in this way soon solidified, and after crystallisation from dilute acetic acid melted at 168° (Found : C = 74·47; H = 5·44; N = 7·44. $C_{23}H_{20}O_3N_2$ requires C = 74·20; H = 5·38; N = 7·53%). This substance is extremely stable towards most reagents. It is not attacked by concentrated mineral acids or alkalis, and is only slowly oxidised by hot acid permanganate. It is not reduced by zinc dust in boiling acetic acid solution.

The *acetyl* derivative was obtained when the quinoxaline (0·4 g.) was boiled with acetic anhydride (5 c.c.) for about 15 minutes. The product was boiled with water to remove excess of the anhydride, and sufficient glacial acetic acid was added to produce a clear solution, which, on cooling, deposited colourless needles, m. p. 190—191° (yield 0·4 g.) (Found : C = 72·33; H = 5·31; N = 6·87. $C_{25}H_{22}O_4N_2$ requires C = 72·46; H = 5·31; N = 6·76%). This substance is readily hydrolysed to the parent quinoxaline (VII) by boiling for a few minutes with aqueous-alcoholic hydrochloric acid, or aqueous-alcoholic sodium hydroxide.

Action of Phosphorus Pentachloride on the Quinoxaline (VII) : *Formation of* 1 : 4-endo-*Keto-2-keto-3* : 3-*diphenyltetrahydroquinoxa-*

line (X) *and other Products.*—No very trustworthy process could be discovered for producing the *endo*-keto-compound; although it could be obtained in a variety of ways, the yield was always small and the results were somewhat uncertain. The reason for this is partly that the compound is attacked by the reagent (phosphorus pentachloride) used in its formation, as is shown by the production of the dichloro-compound (below), and partly that, from the commencement of the reaction, changes occur which cannot lead to the desired compound; this is proved by the evolution of carbonyl chloride and by the formation of the monochloro-compound (below). The most trustworthy method was the following.

The endo-*Keto-compound* (X).—A mixture of the quinoxaline with an equal weight of phosphorus pentachloride was treated with sufficient phosphorus oxychloride to produce a clear solution at 100°. The mixture was then boiled gently for about 20 minutes, cooled, and filtered from the small precipitate produced during the boiling. The chlorides of phosphorus were decomposed with water, and the solid product was collected, dried, and quickly extracted with warm absolute alcohol. The solid which separated from the filtered solution consisted essentially of the *endo*-keto-compound, which, at this degree of purity (m. p. 305—310°), is only sparingly soluble in alcohol. (Hence arises the necessity for extracting quickly; otherwise the compound does not pass into solution with its impurities, and is not crystallised, thus rendering further purification difficult.) Repeated crystallisation from nitrobenzene raises the m. p. to 335° (yield 6%) (Found : C = 77·26; H = 4·59; N = 8·67. $C_{21}H_{14}O_2N_2$ requires C = 77·30; H = 4·29; N = 8·59%).

A *dichloro*-compound, probably 2 : 2-dichloro-1 : 4-*endo*-keto-3 : 3-diphenyltetrahydroquinoxaline (annexed formula), was obtained in the course of the above experiments. In the presence of the impurities which accompany it, it is readily soluble in alcohol, from which, after slight dilution with water, it slowly crystallises. Repeated crystallisation from a mixture of nitrobenzene and ligroin (b. p. 100—120°) yields the pure compound as a micro-crystalline powder, m. p. 246° (decomp.) (Found : C = 66·24; H = 3·90; Cl = 18·46. $C_{21}H_{14}ON_2Cl_2$ requires C = 66·14; H = 3·67; N = 18·64%).

A *monochloro*-compound, probably 3-chloro-2 : 2-diphenyl-1 : 2-dihydroquinoxaline (annexed formula), was isolated in the course of a series of experiments in which benzene was used as a solvent instead of phosphorus oxychloride. It was separated from the product obtained after decomposing with water, by extraction with ether in a Soxhlet's apparatus, and fractional crystallisation
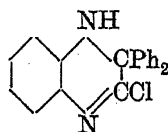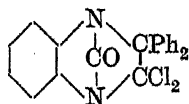
from benzene and from nitrobenzene–ligroin. It accumulated in the more soluble fractions and was ultimately obtained as minute prisms, m. p. 204° (Found : C = 75·07; H = 4·87; Cl = 11·22. $C_{20}H_{15}N_2Cl$ requires C = 75·35; H = 4·71; Cl = 11·15%).

Addition of Ethyl Azodicarboxylate to as-*Diphenylethylene :* *Formation of Ethyl 6 : 6-Diphenylhexahydro-*1 : 2 : 3 : 4-*tetrazine-*1 : 2 : 3 : 4-*tetracarboxylate* (XIII).—Equimolecular quantities of *as*-diphenylethylene and the azo-compound were mixed and kept for about 4 days at the ordinary temperature, when the colour of the azo-compound disappeared and the liquid became extremely viscous. On rubbing with ether, a solid was obtained which separated from chloroform–ligroin in colourless prisms, m. p. 164—166° (Found : C = 58·25; H = 6·18; N = 10·4. $C_{20}H_{28}O_8N_4$ requires C = 59·10; H = 6·06; N = 10·6%). The ether washings yielded unchanged diphenylethylene (about 0·5 mol.), but no other reaction product. The tetrazine derivative is unattacked by cold potassium permanganate and by boiling acetyl chloride. Attempts to hydrolyse it were not successful, deep-seated decomposition taking place, no definite product of which could be recognised.

*Addition of Ethyl Azodicarboxylate to Styrene : Formation of Ethyl 6-Phenylhexahydro-*1 : 2 : 3 : 4-*tetrazine-*1 : 2 : 3 : 4-*tetracarboxylate* (XII).—This reaction was carried out like the preceding one, the colourless, glassy mass partly solidifying on trituration with ether, and styrene (about 0·5 mol.) being recovered from the ether solution after removal of the solid. The substance separated from chloroform–ligroin in colourless prisms, m. p. 133—134°, and had properties similar to those of the preceding compound (Found : C = 52·81; H = 6·15; N = 12·4; M = 466. $C_{20}H_{28}O_8N_4$ requires C = 53·10; H = 6·19; N = 12·4%; M = 452).

*Supplementary Note : Addition of Benzylidene-*p-*nitrobenzylamine to Diphenylketen.*—A solution of the azomethine (6·86 g.) in ether was mixed with a ligroin solution containing 5·55 g. of the keten. The mixture was kept for 24 hours out of contact with air and moisture, and the crystals which had separated were then collected and crystallised from ether and from dilute alcohol, from which large, colourless prisms separated, m. p. 133—134° (Found : C = 77·39; H = 5·22; N = 6·42. $C_{28}H_{22}O_3N_2$ requires C = 77·41; H = 5·07; N = 6·45%). The compound is moderately stable to heat and is non-basic, and is therefore, probably, 2-*keto-*3 : 3 : 4-*tri-phenyl-*1-p-*nitrobenzyltrimethyleneimine* (the *lactam* of β-p-*nitro-benzylamino-*ααβ-*triphenylpropionic acid*),
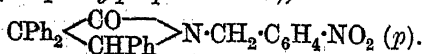
$$CPh_2{<}^{CO}_{CHPh}{>}N{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2 \ (p).$$

LX.—*The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part VI. Products Derived from Halogenated α-Methylglutaric Acids.*

By CHRISTOPHER KELK INGOLD.

IN the previous parts of this series (J., 1921, **119**, 305, and subsequently), comparative experiments have been described the object of which was to furnish a test of the hypothesis, advanced in Part I (*loc. cit.*), that the angle between any two valencies of a carbon atom is determined by the relative molecular volumes of the four groups attached. Theory indicated that on passing through a series of glutaric acids, such as that depicted below, there should be witnessed a gradual closing in of the acetic acid residues as the combined bulk of the substituents attached to the central carbon atom increases :

$$
\begin{array}{ccc}
H\diagdown \quad \diagup CH_2 \cdot CO_2H & CH_3\diagdown \quad \diagup CH_2 \cdot CO_2H & CH_3\diagdown \quad \diagup CH_2 \cdot CO_2H \\
\quad C\diagdown \ 115 \cdot 3° & \quad C\diagdown \ 112 \cdot 5° & \quad C\diagdown \ 109 \cdot 5° \\
H\diagup \quad \diagdown CH_2 \cdot CO_2H & H\diagup \quad \diagdown CH_2 \cdot CO_2H & CH_3\diagup \quad \diagdown CH_2 \cdot CO_2H
\end{array}
$$
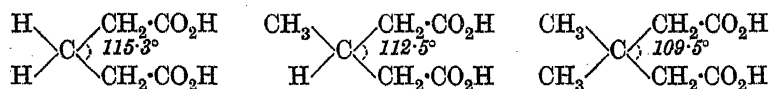
The effect of this convergence has been experimentally realised, and it is manifested by an increasing tendency to *cyclo*propane ring formation by the interaction of atoms or groups attached to the residues in question.

Whilst this work was progressing, it was discovered in the course of a concurrent series of investigations ("Experiments on the Synthesis of the Polyacetic Acids of Methane"; see especially J., 1921, **119**, 1582) that the branching of chains has a very marked effect on a certain class of reactions (Michael's addition-process and its reversion) which appears to be governed to a large extent by spatial factors, the effect of branching being always in the direction suggesting an effective increase of the space-filling power of the group concerned. It seemed desirable, therefore, to include a study of the effect of branching in the comparative investigation which forms the subject of this series, and for this purpose the α-methyl derivative of glutaric acid was selected. If the space-

occupying power of the branched chain $-CH{<}{CH_3 \atop CO_2H}$ is in reality greater than that of the normal chain $-CH_2 \cdot CO_2H$, the angle between the residues in α-methylglutaric acid should be greater than the corresponding angle in glutaric acid itself :

$$\begin{array}{c} H \\ \diagdown \\ \diagup \\ H \end{array} C{\overset{\displaystyle CH{<}{CH_3 \atop CO_2H}}{\underset{\displaystyle CH_2 \cdot CO_2H}{}}}$$

angle greater than 115·3°
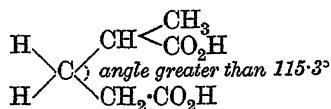
There should therefore be a distinct decrease in the tendency towards *cyclo*propane ring formation from derivatives of α-methylglutaric acid as compared with the tendency displayed by corresponding derivatives of glutaric acid.

*cyclo*Propane ring formation always takes place to a very considerable extent when the monobromination product of a glutaric acid is treated with concentrated alkalis under the standard conditions which have been employed throughout this series of investigations. The principal side reaction is that which gives rise to a hydroxyglutaric acid, whilst small amounts of a glutaconic acid may also be produced. Thus ethyl monobromoglutarate, $CO_2Et \cdot CH_2 \cdot CH_2 \cdot CHBr \cdot CO_2Et$, yields 47% of the ring-acid (I), 16% of the hydroxy-acid (II), and 3% of glutaconic acid (III), the figures representing identified material (total 66%) :

$$CH_2{<}{CH \cdot CO_2H \atop CH \cdot CO_2H} \qquad CH_2{<}{CH(OH) \cdot CO_2H \atop CH_2 \cdot CO_2H} \qquad CH{<}{CH \cdot CO_2H \atop CH_2 \cdot CO_2H}$$

(I.)   (II.)   (III.)
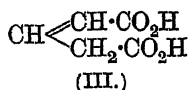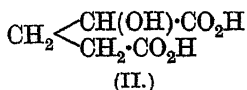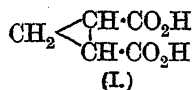
In presence of dilute alkalis, hydroxylation becomes the main reaction, although the formation of small amounts of the ring product can also be observed.

On extending the investigation to α-methylglutaric acid it became clear that derivatives of this substance exhibit a greatly decreased tendency to pass into compounds of the *cyclo*propane series. On monobrominating the acid by way of its chloride and pouring the product into alcohol, two monobromo-esters (IV and V) were obtained, the former in by far the larger quantity :

$$(IV.) \quad CH_2{<}{CHMe \cdot CO_2Et \atop CHBr \cdot CO_2Et} \qquad\qquad CH_2{<}{CBrMe \cdot CO_2Et \atop CH_2 \cdot CO_2Et} \quad (V.)$$
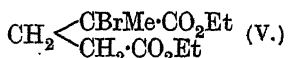
Each of these, on treatment with dilute alkalis under the previously-mentioned standard conditions, gave a hydroxy-acid (VI and VIII), which passed into a γ-lactone (VII, IX) during the manipulation necessary in its isolation. Unlike the formation of the hydroxy-acid (II) from monobromoglutaric ester, these hydr-

oxy-acids were produced quantitatively, without any perceptible accompaniment of ring-formation.

$$\text{(VI.)}\quad CH_2 \Big\langle {}^{CHMe \cdot CO_2H}_{CH(OH) \cdot CO_2H} \quad \longrightarrow \quad CH_2 \Big\langle {}^{CHMe \underline{\qquad} CO}_{CH(CO_2H)-O} \quad \text{(VII.)}$$

$$\text{(VIII.)}\quad CH_2 \Big\langle {}^{CMe(OH) \cdot CO_2H}_{CH_2 \cdot CO_2H} \quad \longrightarrow \quad CH_2 \Big\langle {}^{CMe(CO_2H) \cdot O}_{CH_2 \underline{\qquad} CO} \quad \text{(IX.)}$$
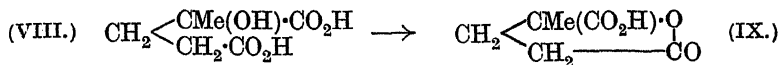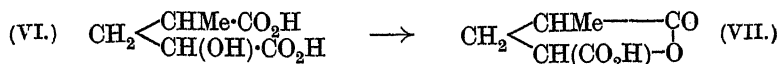
That the main bromination product (IV) should be converted into the hydroxy-acid (VI) without the simultaneous ring formation which characterises the corresponding reaction in the glutaric acid series, appears the more remarkable when count is taken of the lability which tertiary hydrogen usually displays as compared with secondary hydrogen in an otherwise similar situation. The ready elimination of hydrogen bromide from ethyl α-bromo*iso*valerate as compared with ethyl α-bromo-*n*-butyrate :

$$(CH_3)_2CH \cdot CHBr \cdot CO_2Et \longrightarrow (CH_3)_2C\vdots CH \cdot CO_2Et \text{ (easily)}$$
$$CH_3 \cdot CH_2 \cdot CHBr \cdot CO_2Et \longrightarrow CH_3 \cdot CH\vdots CH \cdot CO_2Et \text{ (with difficulty)}$$
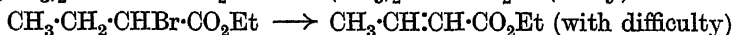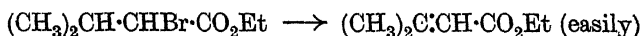
the direct oxidation of β-*iso*propylglutaric acid and the ready chlorination of *iso*amyl chloride :

$$(CH_3)_2CH \cdot CH(CH_2 \cdot CO_2H)_2 \longrightarrow (CH_3)_2C(OH) \cdot CH(CH_2 \cdot CO_2H)_2$$
$$(CH_3)_2CH \cdot CH_2 \cdot CH_2Cl \longrightarrow (CH_3)_2CCl \cdot CH_2 \cdot CH_2Cl$$
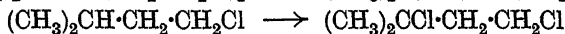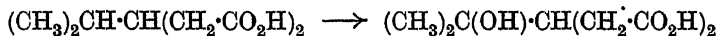
are instances of a general phenomenon which might be expected to render the bromo-ester (IV) *more easily* convertible into a *cyclo*propane derivative than the monobromo-ester of glutaric acid, since in the former case tertiary hydrogen would suffer elimination along with bromine. The observed difference is actually in the opposite direction, an indication that the divergence of the valency directions produced by the spatial requirements of the branched chain is sufficiently great to dominate all minor influences.

When concentrated alkalis were employed under the second set of standard conditions (*loc. cit.*), the formation of the hydroxy-acids took place only to a limited extent. A considerable proportion of the product consisted of *trans*-1-methyl*cyclo*propane-1 : 2-dicarboxylic acid (X), accompanied by a smaller quantity of the corresponding *cis*-acid (XI).

These acids possess the usual properties of geometrical isomerides. The *cis*-acid, on boiling with acetyl chloride, or heating some 20° above its melting point, yields an anhydride (XII), from which it can be regenerated by boiling with water. The *trans*-acid does not yield an anhydride under either of these conditions, but if heated to 180° with acetyl chloride is converted into the anhydride

of the *cis*-acid.   Finally the *cis*-acid can be converted into the *trans*-modification by heating with mineral acids :

$$\underset{_2\ \ \ \ \ H\cdot CO_2H}{CO_2H\dot{.}\dot{C}Me} \quad \xleftarrow{\quad HCl \quad} \quad CH_2\langle\overset{CMe\cdot CO_2H}{\underset{CH\cdot CO_2H}{}} \quad (XI.)$$

$$\text{(AcCl at 180°)} \searrow \qquad CH_2\langle\overset{CMe\cdot CO}{\underset{CH-CO}{}}\rangle O \quad (XII.) \qquad \overset{H_2O}{\underset{heat}{\rightleftarrows}}$$
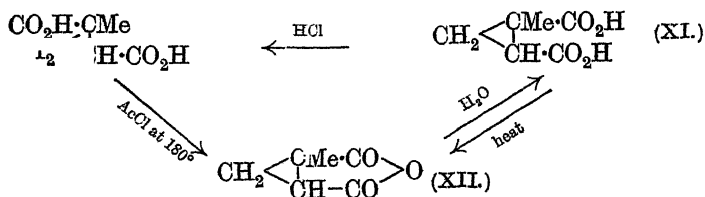
Amongst the products present in smaller quantity were α-methyl-glutaconic acid (γ-methylglutaconic acid) (XIII),

$$CO_2H\cdot CHMe\cdot CH\dot{.}CH\cdot CO_2H \rightleftharpoons CO_2H\cdot CH_2\cdot CH\dot{.}CMe\cdot CO_2H \quad (XIII.)$$
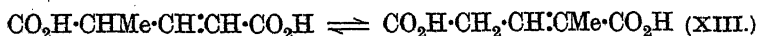
formed by elimination along with bromine of one of the hydrogen atoms of the β-methylene group, and α-methyleneglutaric acid (XIV), evidently produced by an elimination involving a hydrogen atom of the methyl group :

$$CO_2H\cdot C(\dot{.}CH_2)\cdot CH_2\cdot CH_2\cdot CO_2H \quad (XIV.)$$
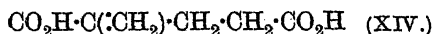
In addition to these products, others were isolated which could have been formed only by the fission of the *cyclo*propane ring in the ring acids mentioned above.   No doubt the first product is methylitamalic acid (XV), which on isolation passes spontaneously into methylparaconic acid (XVI), the fission being analogous to that of caronic acid, which yields terebic acid, and that of *cyclo*propane-1 : 2-dicarboxylic acid (*loc. cit.*), which forms paraconic acid :

$$(X, XI) \longrightarrow \underset{CH_2(OH)\cdot CH\cdot CO_2H}{\overset{CHMe\cdot CO_2H}{}} \longrightarrow \underset{O\cdot CH_2\cdot CH\cdot CO_2H}{\overset{CO-CHMe}{}}$$
$$(XV.) \qquad\qquad\qquad (XVI.)$$
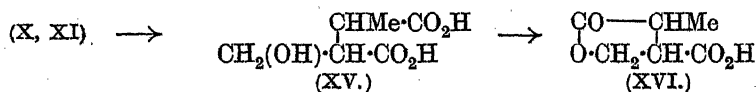
A certain quantity of methylparaconic acid can be isolated, but part of the methylitamalic acid undergoes dehydration in another direction, yielding methylmethylenesuccinic acid (XVII), which in the presence of the alkali is reversibly transformed into a mixture of dimethylfumaric acid (XVIII) and dimethylmaleic acid (XIX), the latter being isolable only in the form of its anhydride (XX) :

$$\underset{\underset{CH_2\dot{.}C\cdot CO_2H}{CHMe\cdot CO_2H}}{(XV.)}\ \downarrow \ \rightleftharpoons \ \left\{ \begin{array}{l} \underset{CH_3\cdot C\cdot CO_2H}{CO_2H\cdot C\cdot CH_3} \ (XVIII.) \\ \underset{CH_3\cdot C\cdot CO_2H}{CH_3\cdot C\cdot CO_2H} \end{array} \right. \longrightarrow \underset{CH_3\cdot C\cdot CO}{\overset{CH_3\cdot C\cdot CO}{}}\rangle O$$

(XVII.)   (XIX.)   (XX.)
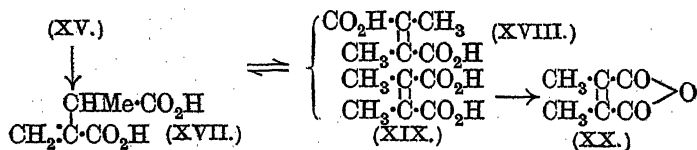
Although the quantitative aspect of these reactions was studied with some care, it was not found possible to recover much more

than 70% of the material in the form of pure isolated products. During the separation and purification of the individual substances, numerous small losses were practically unavoidable, so that the deficit can be accounted for without supposing that any product of importance has been missed. The following table represents the best results obtained after a considerable number of preliminary trials.

TABLE I.

	Per cent.
Lactone of γ-hydroxy-α-methylglutaric acid (VII)	23
Lactone of α-hydroxy-α-methylglutaric acid (IX)	5
α-Methylglutaconic acid (normal form) (XIII)	3
α-Methyleneglutaric acid (XIV)	3
cis-1-Methylcyclopropane-1 : 2-dicarboxylic acid (XI)	5
trans-1-Methylcyclopropane-1 : 2-dicarboxylic acid (X)	20
Methylparaconic acid (XVI) *	6
Methylenemethylsuccinic acid (XVII) *	3
Dimethylfumaric acid (XVIII)	3
Dimethylmaleic anhydride (XX)	2
Total isolated...	73

* Part converted into dimethylmaleic anhydride during separation and weighed in that form.

In computing these results for the purpose of arriving at a comparison of the relative tendencies towards ring formation in the glutaric acid series and in the α-methylglutaric acid series, it is legitimate to count, in place of each product of ring-fission, an equivalent amount of the ring acid. The following figures (Table II) are obtained in this way from those of Table I and the table of results given in Part I (*loc. cit.*).

TABLE II.

Products.	Derivatives from	
	Glutaric acid.	α-Methylglutaric acid.*
α-Hydroxyglutaric acids	16 per cent.	28 per cent.
Glutaconic acids	3 ,,	3 ,,
cycloPropane acids	47 ,,	39 ,,
	66 ,,	70 ,,

* The 3% of methyleneglutaric acid, the formation of which is probably due to a fourth side-reaction, is neglected.

From this table it is evident that the quantity of glutaconic acids produced is in each case small and of a similar order of magnitude. Hence for the comparison of the extent to which cyclopropane ring formation takes place in competition with hydroxylation we may regard the glutaconic acids as representing material put out of action. Calculating the proportions of hydroxylation products to ring-acids as percentages of the material

identified as having passed into one or other of these two forms, we obtain the following figures, which plainly mark the decreased tendency to ring closure produced by the branching of the acetic acid residue :

TABLE III.

Products.	Derivatives from	
	Glutaric acid.	α-Methylglutaric acid.
Hydroxylation	25 per cent.	43 per cent.
Ring-formation	75 ,,	57 ,,
	100 ,,	100 ,,

It remains to be added that no trace of *cyclo*butane-1 : 3-dicarboxylic acid (XXI) could be detected, although its formation from the bromo-ester (IV) might be expected to take place according to the scheme

$$\text{(IV.)} \quad CH_2{<}{\overset{CHBr \cdot CO_2Et}{CO_2Et \cdot CH \cdot CH_3}} \quad \xrightarrow{\text{(KOH)}} \quad CH_2{<}{\overset{CH \cdot CO_2H}{\underset{CO_2H \cdot CH}{}}}{>}CH_2 \quad \text{(XXI.)}$$
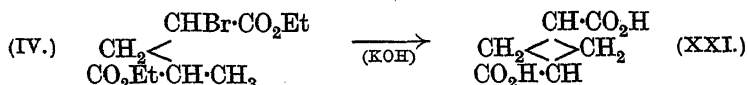
if the mechanism of the formation of *cyclo*butane-1 : 3-dicarboxylic ester from α-chloropropionic ester by the action of sodium ethoxide (Markovnikov and Krestovnikov, *Annalen*, 1881, **208**, 333) is, as might naturally be supposed, the following :

$$\overset{CH_3 \cdot CHCl \cdot CO_2Et}{\underset{CO_2Et \cdot CHCl \cdot CH_3}{+}} \xrightarrow{\text{(NaOEt)}} CH_2{<}{\overset{CHCl \cdot CO_2Et}{CO_2Et \cdot CH \cdot CH_3}} \xrightarrow{\text{(NaOEt)}} CH_2{<}{\overset{CH \cdot CO_2Et}{\underset{CO_2Et \cdot CH}{}}}{>}CH_2$$

$$\text{(XXII.)} \qquad \text{(XXIII.)}$$
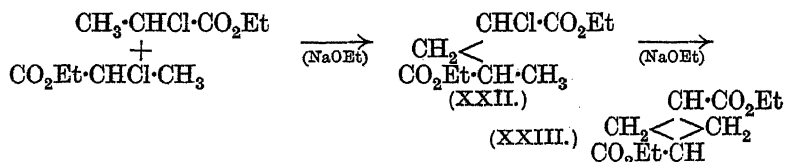
for the hypothetical intermediate product (XXII) is the chlorine analogue of the bromo-ester (IV). Moreover the chloro-compound (XXII) has been prepared synthetically, by the chlorination of α-methylglutaric acid, and all attempts to convert it into the *cyclo*butane ester (XXIII) by the agency of sodium ethoxide have hitherto failed.

It has been thought right to mention these negative results here, as, although the mechanism of the Markovnikov-Krestovnikov reaction is at present under investigation, the matter is of such complexity that it may well baffle enquiry for a considerable time.

EXPERIMENTAL.

The α-methylglutaric acid required for these experiments was prepared by condensing ethyl β-iodopropionate with ethyl sodiomethylmalonate and hydrolysing the product with hydrochloric

acid (Auwers, *Annalen*, 1896, **292**, 209). Instead of distilling the residue obtained by complete evaporation of the hydrochloric acid solution, as Auwers recommends, the solution was concentrated to a small bulk and kept for 16 hours to crystallise, when nearly the whole of the α-methylglutaric acid separated. The syrupy mother-liquors were evaporated to dryness and distilled under diminished pressure, when a little carbon dioxide was evolved and the distillate set to a crystalline mass consisting of practically pure α-methylglutaric acid. The partial dehydration of this acid on distillation, noticed by Auwers, was not observed when only a small quantity was distilled at once, as in the method of preparation employed. The yield in the condensation was 60% of the theoretical (the principal by-product being ethyl acrylate), and the yield in the hydrolysis, 88% of the theoretical.

(A) *Monohalogenation of α-Methylglutaric Acid.*

Bromination.—A mixture of α-methylglutaric acid (80 g.) and thionyl chloride (110 c.c.) was warmed until no more sulphur dioxide was generated. The product was kept at 40°, first for 40 hours while 32 c.c. of bromine were added, then for 24 hours, and the reaction was completed by keeping at 60° for a few hours.

Methyl γ-bromo-α-methylglutarate,

$$CO_2Me \cdot CHBr \cdot CH_2 \cdot CHMe \cdot CO_2Me,$$

was prepared by pouring the crude bromination product into methyl alcohol and collecting in ether after the addition of water. Traces of acid products having been removed with aqueous sodium carbonate, the extract was washed with water, dried, and evaporated, the residual oil being carefully fractionated to remove small amounts of unbrominated and dibrominated ester. After several distillations, the ester was obtained as an oil, b. p. 139—144°/14—15 mm. (Found : Br $= 31 \cdot 4$. $C_8H_{13}O_4Br$ requires Br $= 31 \cdot 6\%$).

Ethyl γ-bromo-α-methylglutarate (IV) was prepared like the preceding ester and boiled at 145—150°/14—15 mm. (Found : Br $= 28 \cdot 8$. $C_{10}H_{17}O_4Br$ requires Br $= 28 \cdot 6\%$).

Chlorination.—The chloride of the acid, prepared as for the preceding experiments, was kept at 40°, and treated with one-fifth of the quantity of chlorine theoretically required for monochlorination on each of six successive days. After a further 48 hours, part of the product was poured into methyl alcohol and part into ethyl alcohol.

Methyl γ-chloro-α-methylglutarate,

$$CO_2Me \cdot CHCl \cdot CH_2 \cdot CHMe \cdot CO_2Me,$$
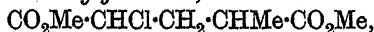
was obtained as an oil, b. p. 120—124°/15—16 mm. (Found : Cl $= 17 \cdot 2$. $C_8H_{13}O_4Cl$ requires Cl $= 17 \cdot 0\%$). The *ethyl* ester also was

an oil, b. p. 128—130°/14—16 mm. (Found : Cl = 14·8. $C_{10}H_{17}O_4Cl$ requires Cl = 14·9%).

Iodination.—The chloro-esters were each digested for 2 hours with an equivalent of finely divided sodium iodide in alcoholic suspension, and the oily product was collected in ether after pouring into water.

Methyl α-*iodo-*α-*methylglutarate,* $CO_2Me \cdot CHI \cdot CH_2 \cdot CHMe \cdot CO_2Me$, has b. p. 174—176°/12—13 mm. (Found : I = 42·5. $C_8H_{13}O_4I$ requires I = 42·3%). The *ethyl* ester has b. p. 194—197°/12—13 mm. (Found : I = 38·7. $C_{10}H_{17}O_4I$ requires I = 38·7%).

The experiments described below show that each of these esters contains as an impurity a small amount of the isomeric α-halogen-α-methylglutaric ester (type V).

(B) *Action of Dilute Alkalis on the Monobromo-ester : Formation of the Lactones of* γ-*Hydroxy-*α-*methylglutaric and* α-*Hydroxy-*α-*methylglutaric Acids.*

The monobromo-ester (section A) was boiled with 4·5 equivalents of 2N-aqueous sodium carbonate for 20 hours. The product was concentrated, acidified with hydrochloric acid, evaporated completely to dryness, and extracted with acetone.

Lactone of α-*Hydroxy-*α-*methylglutaric Acid* (IX).—The residue obtained on evaporating the acetone was boiled with a suspension of calcium hydroxide. The filtered solution, on concentrating and cooling, deposited a calcium salt, fine needles, nearly insoluble in cold water (yield about 4%). The lactone regenerated from the calcium salt by the action of hydrochloric acid was extracted with ethyl acetate and crystallised from a mixture of this solvent with light petroleum, from which it separated in small prisms, m. p. 71° (Found : C = 50·1 ; H = 5·7. $C_6H_8O_4$ requires C = 50·0 ; H = 5·5%).

Its constitution was established by oxidation with warm alkaline permanganate (3%), when succinic acid was obtained unaccompanied by any methylsuccinic acid.

The *ammonium* salt separated from a small amount of alcohol in clusters of small needles (Found : C = 44·6 ; H = 7·2. $C_6H_{11}O_4N$ requires C = 44·7 ; H = 6·8%). The *silver* salt was obtained from the ammonium salt as a rather soluble, white precipitate (Found : Ag = 42·7. $C_6H_7O_4Ag$ requires Ag = 43·0%).

α-*Hydroxy-*α-*methylglutaric Acid* (VIII).—This acid does not appear to be stable in the free state, but its salts are formed by the action of alkalis on the lactone. Attempts to regenerate the acid led to the lactone.

The *barium* salt, prepared by boiling the lactone with excess of barium hydroxide, formed microscopic prisms, which were dried

in a vacuum at 120° (Found : Ba = 45·8. $C_6H_8O_5Ba$ requires Ba = 46·2%). The *silver* salt was prepared from the barium salt (Found : Ag = 57·5. $C_6H_8O_5Ag_2$ requires Ag = 57·5%).

Lactone of γ-Hydroxy-α-methylglutaric Acid (VII).—The material remaining in solution after the separation of the sparingly soluble calcium salt appeared to be homogeneous, consisting of a readily soluble salt crystallising from concentrated solution in separate leaflets or crusts. On dissolving this in hydrochloric acid and extracting with ethyl acetate, a lactone, b. p. 185—187°/14 mm., was obtained (Found : C = 50·0 ; H = 5·6. $C_6H_8O_4$ requires C = 50·0 ; H = 5·5%).

Its constitution was established by oxidation with warm 3% alkaline permanganate, when methylsuccinic acid was obtained.

The *ammonium* salt separated from ethyl acetate in rosettes of needles (Found : C = 44·3 ; H = 7·0. $C_6H_{11}O_4N$ requires C = 44·7 ; H = 6·8%). The *silver* salt was obtained from the ammonium salt (Found : Ag = 42·9. $C_6H_7O_4Ag$ requires Ag = 43·0%).

The *ethyl* ester, obtained both from the silver salt and ethyl iodide, and directly from the bromo-ester (IV) by incomplete hydrolysis with sodium carbonate, is a mobile liquid, b. p. 170—172°/14—15 mm., and when prepared from the bromo-ester can easily be separated from the accompanying lactonic acid by distillation (Found : C = 55·6 ; H = 7·2. $C_8H_{12}O_4$ requires C = 55·8 ; H = 7·0%).

γ-Hydroxy-α-methylglutaric Acid (VI).—The salts of this acid are formed by the action of alkalis on the lactone, but attempts to regenerate the free hydroxy-acid led to the lactonic acid. The *barium* salt, prepared from the lactone and the theoretical amount of barium hydroxide, separated from a fairly concentrated solution in leaflets, which were dried at 120° (Found : Ba = 45·9. $C_6H_8O_5Ba$ requires Ba = 46·2%). The *silver* salt was prepared from the barium salt (Found : Ag = 57·2. $C_6H_8O_5Ag_2$ requires Ag = 57·5%).

(C) *Action of Concentrated Alkalis on the Monobromo-ester : Formation of the Lactones of α- and γ-Hydroxy-α-methylglutaric Acid, α-Methyleneglutaric Acid, Normal α-Methylglutaconic Acid, cis- and trans-1-Methylcyclopropane-1 : 2-dicarboxylic Acid, Methylparaconic Acid, Methylenesuccinic Acid, Dimethylfumaric Acid and Pyrocinchonic Anhydride.*

The bromo-ester (105 g.) (Section A) was heated to 100° and poured into 500 c.c. of boiling 6N-methyl-alcoholic potassium hydroxide. The product was evaporated several times with water, acidified with hydrochloric acid, and distilled for a short time under diminished pressure.

Pyrocinchonic Anhydride (XX).—The distillate on extraction with ether yielded an oil the major portion of which distilled at 230—235° and then set to a mass of crystals, which, after crystallisation from ether–light petroleum, melted at 96° and were identified as pyrocinchonic anhydride (Found :   C = 56·7 ;   H = 5·0.   Calc., C = 57·1 ;   H = 4·8%).

trans-1-*Methyl*cyclo*propane*-1 : 2-*dicarboxylic   Acid*   (X).—The hydrochloric acid solution remaining after the distillation was evaporated under reduced pressure, and the organic acids were extracted from the dried residue with acetone.   The residue from the acetone was shaken for 24 hours with an aqueous suspension of precipitated calcium carbonate, and the filtered solution concentrated and allowed to crystallise.   The calcium salts were collected, dissolved in just sufficient hydrochloric acid, and distilled in steam, until no more pyrocinchonic anhydride appeared in the distillate and until the residue no longer reduced cold alkaline permanganate.   Since the pyrocinchonic anhydride had been previously removed from the original mixture, the further quantity obtained in this way was probably formed during the distillation from methylenemethylsuccinic acid (XVII, see below).   On strongly acidifying and extracting with ether, the residue yielded fairly pure *trans*-ring acid, which, after crystallisation from acetone–benzene, formed stout prisms, m. p. 168° (Found :   C = 49·7 ; H = 5·6. $C_6H_8O_4$ requires C = 50·0 ;   H = 5·6%).

The ring-acid is remarkably stable towards alkaline permanganate, and it can be boiled in an open tube with only slight decomposition. On heating at 180° with acetyl chloride, it is converted into the anhydride of the *cis*-acid (*q.v.*).

The *calcium* salt (above) formed small plates, which were dried at 120° before analysis (Found :   Ca = 22·1. $C_6H_6O_4Ca$ requires Ca = 22·0%).   The *silver* salt was prepared from the calcium salt (Found :   Ag = 60·1. $C_6H_6O_4Ag_2$ requires Ca = 60·3%).

The *di-*p-*toluidide*, produced by boiling the acid with *p*-toluidine and washing the product with dilute hydrochloric acid, separated from alcohol in long needles, m. p. 255—260° (Found :   C = 74·3 ; H = 7·0. $C_{20}H_{22}O_2N_2$ requires C = 74·5 ;   H = 6·9%).

Lactone of 1-*Hydroxy*-1-*methylglutaric Acid* (IX).—The filtrates from the calcium salts were worked up for organic acids, which were converted into their ammonium salts and thence into their silver salts.   The latter were digested with an alcoholic solution of benzyl iodide, and the filtered solution was poured into water and extracted with ether.   The residue from the ether was distilled up to 240°/15 mm., and the distillate hydrolysed with dilute hydrochloric acid.   The solution was then worked up for organic acids,

which were converted into their calcium salts by boiling with an excess of calcium hydroxide suspended in water. After 24 hours, the solution was filtered and the residue decomposed with the smallest possible excess of sulphuric acid. The filtrate from the calcium sulphate, on evaporation to a small bulk and extraction with ethyl acetate after the addition of hydrochloric acid, yielded a solid product, which, after crystallisation from ethyl acetate–ligroin, gave crystals, m. p. 71°, of the lactone previously described (Found : C = 50·2; H = 5·6%).

Methylparaconic Acid (XVI).—The alkaline solution of calcium salts on evaporation to a small bulk yielded a salt which, on decomposition with hydrochloric acid, gave methylparaconic acid, m. p. 104°; this was extracted with ethyl acetate and crystallised from ethyl acetate–ligroin. The substance had all the properties of methylparaconic acid, and it was identified by analysis (Found : C = 49·9; H = 5·6. Calc., C = 50·0; H = 5·5%), conversion into pyrocinchonic anhydride, and into the *barium* salt of *methyl-itamalic acid*, which was prepared using an excess of barium hydroxide and dried at 120° (Found : Ba = 46·1. $C_6H_8O_5Ba$ requires Ba = 46·2%). The ethyl acetate–ligroin mother-liquors yielded a further small quantity of the lactone, m. p. 71° (above).

Lactone of γ-Hydroxy-α-methylglutaric Acid (VII).—The most soluble calcium salts evidently still contained a little calcium methylitamalate, because on isolating the organic acids and distilling under a short reflux a small amount of pyrocinchonic anhydride was obtained. The residue from this distillation, on distillation without reflux and under reduced pressure, gave the lactone of γ-hydroxy-α-methylglutaric acid (Found : C = 49·8; H = 5·6%), identical with that previously described.

Dimethylfumaric Acid (XVIII).—The less volatile benzyl esters were hydrolysed as before and the recovered acid was boiled for some hours with acetyl chloride (6 parts). The product was distilled up to 150°/14 mm. in a current of dry air, and the less volatile portion boiled with water and animal charcoal. The solution, after filtering and concentrating, was neutralised with ammonia and treated with an excess of calcium chloride. After 24 hours, the calcium salt was collected, and was proved to be that of the *trans-cyclo*propane acid. The filtrate on boiling yielded another calcium salt, that of dimethylfumaric acid, which was isolated and crystallised from water, m. p. 240° (Found : C = 49·8; H = 5·5. Calc., C = 50·0; H = 5·6%). It was identified by conversion into dimethylmaleic anhydride.

Normal α-Methylglutaconic Acid (XIII).—The volatile anhydrides were shaken for a few seconds with cold dilute sodium carbonate,

and the acids were regenerated from the aqueous layer. The acid so obtained, which was purified by crystallisation from concentrated hydrochloric acid, was identified by its m. p., 142°, by analysis (Found : C = 50·1; H = 5·7. Calc., C = 50·0; H = 5·5%), and by direct comparison with a genuine specimen as the less fusible form of α-methylglutaconic acid.

Methylenemethylsuccinic Acid (XVII).—The neutral anhydrides were boiled with sodium hydroxide and the neutralised solution was treated with calcium chloride. The sparingly soluble calcium salt was collected and converted into the free acid, which was crystallised from water and from ethyl acetate–chloroform, and identified by its melting point, 151°, analysis (Found : C = 49·9; H = 5·8. Calc., C = 50·0; H = 5·5%), and properties as methyl-enemethylsuccinic acid.

cis-1-*Methyl*cyclo*propane*-1 : 2-*dicarboxylic Acid* (XI).—The soluble calcium salts were crystallised in three approximately equal fractions, from each of which the acids were regenerated. The first fraction gave nearly pure *cis*-ring acid, and a further quantity was obtained from the mixture of acids regenerated from the second fraction by crystallising from benzene–acetone. The acid crystallises from mixtures of these solvents in dense prisms, m. p. 142°; the fused acid evolves water vapour at about 160° and gives the anhydride (Found : C = 49·8; H = 5·6. $C_6H_8O_4$ requires C = 50·0; H = 5·5%). On heating with hydrochloric acid, it is partly converted into the *trans*-acid.

The *anhydride* (XII), which may be obtained either by heating the *trans*-acid with excess of acetyl chloride at 180° for 3 hours, or by boiling the *cis*-acid with acetyl chloride, or by heating the *cis*-acid at 160° in an open tube, is a colourless, mobile liquid, b. p. 154—157°/19—20 mm. (Found : C = 56·9; H = 5·0. $C_6H_6O_3$ requires C = 57·1; H = 4·8%). It is insoluble in cold sodium hydrogen carbonate, but soluble in boiling water or alkalis, giving the *cis*-acid or its salts.

α-*Methyleneglutaric Acid* (XIV).—This acid was obtained from the most soluble calcium salts, and, mixed with the *cis*-ring acid, from the intermediate fraction. It was purified by crystallisation from benzene–acetone, and identified by its m. p. (130°), analysis (Found : C = 50·3; H = 5·6. Calc., C = 50·0; H = 5·5%), and properties.

LXI.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXIV. Further Experiments on the Walden Inversion.*

By JOSEPH KENYON, HENRY PHILLIPS, and HAROLD GEORGE TURLEY.

IN Part XVII (J., 1923, **123**, 44) of these investigations, it was shown that the *p*-toluenesulphonate of *d*-benzylmethylcarbinol reacts in alcoholic solution with potassium acetate to form a lævorotatory benzylmethylcarbinyl acetate the rotatory power of which indicates that inversion of configuration to the extent of 98·7% has taken place. In this new type of Walden inversion the change of configuration, remarkable for its completeness, occurred during a single chemical reaction, and hence the reactions of sulphonic esters of optically active hydroxy-compounds should prove an eminently suitable means of investigating the obscure phenomena included in the term Walden inversion.

In order to compare the configurative changes which occur during the reactions of the *p*-toluenesulphonate of an α-hydroxy-acid with those which are known to occur during the reactions of other—especially halogen—derivatives of these compounds, a study has been made of the reactions of ethyl " *d* "-α-*p*-toluenesulphonoxypropionate.*

This sulphonate reacts readily in alcoholic solution with potassium salts of carboxylic acids. When potassium acetate or phenylacetate was used, inversion analogous in degree to those described in Part XVII was obtained, but the use of potassium benzoate led to the formation of the benzoyl derivative of ethyl " *l* "-lactate with a rotatory power of opposite sign but of *equal* magnitude, within the limits of experimental error, to that of the benzoyl derivative of ethyl " *d* "-lactate prepared by the action of benzoyl chloride on the same specimen of ethyl " *d* "-lactate as that from which the *p*-toluenesulphonate had been obtained. These reactions may be represented as follows :—
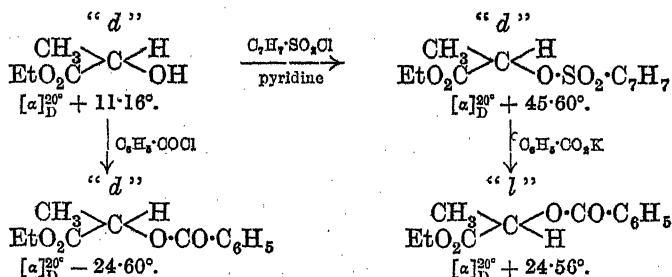
* Throughout this paper, lævorotatory lactic acid is assumed to be dextro in configuration and the signs " *d* " and " *l* " are used to represent configurations.

Now it is reasonable to assume that, in the preparation of the ethyl "d"-α-p-toluenesulphonoxypropionate by the interaction of ethyl "d"-lactate and p-toluenesulphonyl chloride in pyridine solution, no change of configuration occurs, since the reaction involves merely the replacement of the hydrogen of the hydroxyl group and thus disturbance of the valencies of the asymmetric carbon atom is unlikely.

For the same reason it can be assumed that benzoyl chloride reacts with ethyl "d"-lactate without producing configurative change, and hence it follows that the complete inversion of configuration observed occurs at the second stage of the process, namely, during the interaction of the potassium benzoate and ethyl "d"-α-p-toluenesulphonoxypropionate. Thus an "abnormal" reaction unaccompanied by any side reaction has been demonstrated for the first time.

The results are tabulated below :—

	Rotatory power, $[\alpha]_D^{20°}$, of the product formed by the interaction of :		
Acyl product.	Acid chloride and ethyl "d"-lactate.	Potassium salt and sulphonate.	Amount of inversion. %.
Ethyl α-benzoyloxypropionate	$-24.60°$	$+24.56°$	100
Ethyl α-phenylacetoxypropionate	$+38.54$	-37.61	99
Ethyl α-acetoxypropionate	$+51.54$	-47.63	96

The mechanism of such reactions has been discussed in Part XVII and, stated briefly, the conclusion drawn was that they were initiated by the addition of the salt, through the carbonyl oxygen atom of its carboxyl group, to the asymmetric carbon atom which had been rendered unsaturated by the mutual interaction of the α-hydrogen atom and the p-toluenesulphonoxy-group. Such a mode of interaction is considered applicable to the reactions described above. Further, it is not considered likely that the small loss of rotatory power which accompanied the preparation of the acetate and phenylacetate is due to " catalytic " racemisation, but that it arises through the occurrence of a concurrent direct reaction which does not result in configurative change of the molecule (compare Senter, Drew, and Martin, J., 1918, **113**, 151, and, in a slightly different connexion, McKenzie and Clough, J., 1910 **97**, 1017; Holmberg, *Arkiv Kem. Min. Geol.*, 1916, No. 8, 6).

The fundamental question then arises as to what determines the relative proportions of each type of reaction. To this the experimental results so far obtained do not give a definite answer. As

far as can be seen, however, variation within moderate limits in the constitution of the ester portion of the sulphonate molecule does not materially affect the relative proportions of the direct and indirect displacements. It seems probable that, under the experimental conditions used, the unsaturated nature of the CO_2K group of potassium acetate and more especially of potassium benzoate may be the main factor which favours the indirect reaction.

The p-toluenesulphonyl derivative of ethyl lactate reacts with lithium chloride, sodium bromide, or potassium iodide in alcoholic solution according to the general equation :

$$CH_3 \cdot CH(O \cdot SO_2 \cdot C_7H_7) \cdot CO_2Et + MX =$$
$$CH_3 \cdot CHX \cdot CO_2Et + MO \cdot SO_2 \cdot C_7H_7.$$
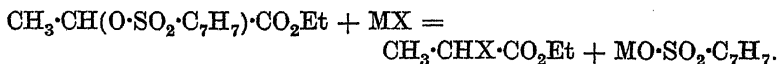
The results are tabulated below, the first column giving the rotatory power, $[\alpha]_D^{20°}$, of the ethyl lactate from which the sulphonate was prepared.

$[\alpha]_D^{20°}$	MX.	Ester obtained.	Yield %.	Obs. rot. of product.* $l = 100$.
− 7·26°	LiCl	α-Chloropropionate.	87	$\alpha_D^{25°}$ +3·02°
+11·29	NaBr	α-Bromopropionate.	94	$\alpha_D^{16°}$ −0·80
+11·29	KI	α-Iodopropionate.	100	$\alpha_D^{20°}$ −0·20

* All observed rotations recorded in this paper are for 100 mm., except where otherwise indicated.

In all three cases a change of sign takes place, but the great loss of rotatory power which occurs is in marked contrast to the small loss which takes place during the preparation of the acyl derivatives.

Whilst the increase in the proportion of the direct reaction cannot be easily explained by the assumption that both the direct and the indirect displacement reaction are "ionic" in character, it does seem to indicate that the nature of the ionised salt (in these cases halides instead of carboxylates) plays an important part.

By the interaction of magnesium phenyl bromide and ethyl p-toluenesulphonate (Ferns and Lapworth, J., 1912, **101**, 273) and β-chloroethyl p-toluenesulphonate (Gilman and Beaber, J. Amer. Chem. Soc., 1923, **45**, 839), ethylbenzene and β-chloroethylbenzene, respectively, have been obtained in small yield.

A similar reaction, carried out with the p-toluenesulphonyl derivative of optically active ethyl lactate, gave, not the expected α-phenylpropionic ester, but α-bromopropionic ester in good yield and having a high rotatory power. In view of the surprising nature of this result, a hitherto undescribed type of reaction, the action of other Grignard reagents on the sulphonate has been investigated, with the following results ($\alpha_D^{25°}$ denotes the rotation of the ethyl lactate from which the sulphonate was prepared) :—

$$MgR \cdot X + CH_3 \cdot CH(O \cdot SO_2 \cdot C_7H_7) \cdot CO_2Et =$$
$$CH_3 \cdot CHX \cdot CO_2Et + R \cdot MgO \cdot SO_2 \cdot C_7H_7.$$
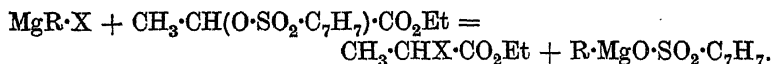
a_D .	Reactant.	Product.	Rotation of product.
$-6.94°$ *	EtO·MgI	CH$_3$·CHI·CO$_2$Et	$a_D^{22°} +1.88°$
	MgEtBr	CH$_3$·CHBr·CO$_2$Et	$a_D^{20°} +17.80°$
	MgPhBr	,,	$a_D^{20°} +15.84°$

* Phosphorus pentabromide reacts with the same sample of ethyl lactate to give α-bromopropionic ester with $a_D^{20°} +20.6°$.

The action of alkylating reagents on the p-toluenesulphonyl derivative of ethyl lactate was attended by marked loss of rotatory power; on the contrary, the action of sodium phenoxide did not involve loss of rotatory power to the same extent.

	Reactant in ethyl alcohol.	Ethyl ester formed.	Rotation of product.
i. Sulphonate from ethyl lactate, $a_D^{22°} +11.52°$.	NaOEt	α-Ethoxy-propionate	$\pm 0°$
ii. Sulphonate from ethyl lactate, $a_D^{25°} -6.94°$.	K$_2$CO$_3$	α-Ethoxy-propionate	$a_D^{20°} - 8.7$
iii. Sulphonate from ethyl lactate, $a_D^{22°} +11.52°$.	NaO·C$_6$H$_5$	α-Phenoxy-propionate	$a_D^{23°} -14.56$
iv. Sodium derivative from ethyl lactate, $a_D^{22°} +11.52°$	EtO·SO$_2$·C$_7$H$_7$	α-Ethoxy-propionate	$a_D^{21°} + 1.94$

It is suggested that the formation of ethyl α-ethoxypropionate in experiments (i), (ii), and (iv) is accompanied by the double decomposition of the reactants according to the following scheme,

$$\text{``}d\text{''}$$

ethyl "l"-α-ethoxypropionate

ethyl "d"-α-ethoxypropionate
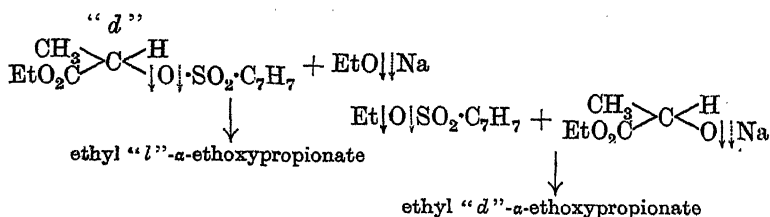
in which the dotted arrows indicate the points of dissociation when double decomposition occurs, whilst the normal arrows indicate the points of interaction which lead to the formation of ethyl α-ethoxy-propionate. It will be seen that ethyl α-ethoxypropionate may be produced by the substances on the left-hand side of the scheme with inversion of configuration, whilst its production from those on the right-hand side is unlikely to be attended with configurative change. It is therefore to be expected that the ethyl α-ethoxy-propionate obtained, using either "d"-α-p-toluenesulphonoxy-propionic ester and sodium ethoxide or ethyl p-toluenesulphonate and the sodium derivative of ethyl "d"-lactate, will be of low rotatory power. A further cause of loss of rotatory power in

experiment (iv) is to be found in the racemisation which occurs when ethyl " d "-lactate is treated with sodium. Racemisation may also occur in the other experiments owing to the formation of the sodium derivative of ethyl lactate as indicated in the above scheme.

The high rotatory power of the phenyl ether produced in experiment (iii) can be accounted for by using the above suggestion.

$$\overset{\text{"}d\text{"}}{\underset{EtO_2C}{\overset{CH_3}{>}}C\overset{H}{\underset{\downarrow O \downarrow \cdot SO_2 \cdot C_7H_7}{<}}} + C_6H_5 \cdot O \|Na \rightleftharpoons \qquad \text{"}d\text{"}$$

$$\downarrow \qquad C_6H_5 \cdot O|SO_2 \cdot C_7H_7 + \underset{EtO_2C}{\overset{CH_3}{>}}C\overset{H}{\underset{O|Na}{<}}$$

ethyl " l "-α-phenoxypropionate
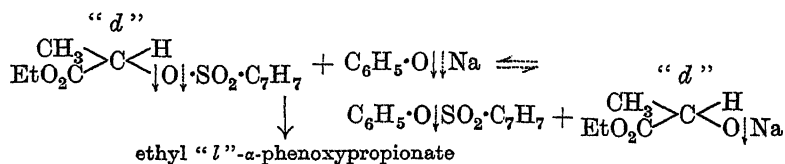
In this instance, the compounds on the right-hand side of the scheme do not react to produce ethyl α-phenoxypropionate, since under the experimental conditions employed, phenyl p-toluene-sulphonate cannot rupture at its O—C linking, a possibility which was foreseen by Ferns and Lapworth (*loc. cit.*), and proved experimentally in Part XVII of these investigations. Hence the ethyl α-phenoxypropionate arises solely through the interaction of the " d "-α-p-toluenesulphonoxypropionate and sodium phenoxide and is therefore more likely to be isolated in a state of optical purity.

A series of experiments on the hydrolysis of a lævorotatory ethyl α-p-toluenesulphonoxypropionate was also carried out and the results are tabulated below.

Rotation, $\alpha_D^{20°}$, of the ethyl lactate from which the sulphonate was prepared.	Hydrolytic agent acting on the sulphonate.	Solvent.	Final products * (ethyl esters).	Rotation of products.	Approximate percentage loss of rotatory power.
1. —7·26°	NaOH	Water	Lactate	$\alpha_D^{20°}$ — 5·2°	30
2. †	Ag₂O	,,	,,	$\alpha_D^{22°}$ — 5·84	20
3.	KOH	Alcohol	(i) Lactate (1 part)	$\alpha_D^{20°}$ —19·56 (as acetate)	40
			(ii) Ethoxy-propionate (2 parts)	$\alpha_D^{20°}$ — 14·00	80
4. —6·94	K₂CO₃	,,	(*a*) Ethoxy-propionate (1 part)	$\alpha_D^{21°}$ — 8·72	90
			(*b*) Lactate (2 parts)	$\alpha_D^{21°}$ + 4 (as acetate)	90

* The products were obtained in the form of their salts with the bases employed. These were re-esterified, using ethyl p-toluenesulphonate, whilst, in 3 and 4, acetylation of the ethyl lactate was necessary in order to afford means of separating this compound from the ethyl α-ethoxypropionate simultaneously produced.

† This reaction was carried out on α-p-toluenesulphonoxypropionic acid prepared from ethyl lactate of the rotatory power indicated.

In reality, the experiments were hydrolyses of the silver and potassium salts of " l "-α-p-toluenesulphonoxypropionic acid in the presence of a molecular proportion of the hydrolytic reagent.

The reagents employed were ideally suited to promote the disruption of the sulphonic ester at its O—S linking, and hence without inversion of configuration, but it is important to notice that the interchange in this instance is *irreversible*.

$$\underset{EtO_2C}{\overset{CH_3}{}}>C<\underset{O\downarrow\cdot SO_2\cdot C_7H_7}{\overset{H}{}} + 2KOH \longrightarrow \underset{KO_2C}{\overset{CH_3}{}}>C<\underset{O\downarrow K}{\overset{H}{}} + 2HO\cdot SO_2\cdot C_7H_7.$$
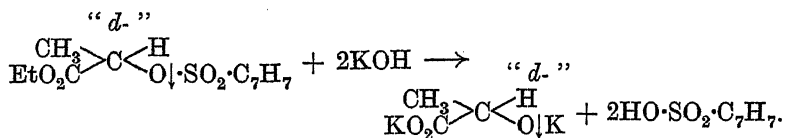
Moreover, it must be remembered that this view of the reaction is in no way opposed to the mode of interaction of sulphonic esters described in Part XVII; the reaction arises in a similar manner to the direct reaction and takes an alternative course. The indirect reaction which produces configurative change of the molecule may thus be completely overshadowed by the combined effects of the direct and the hydrolytic reaction. There are, however, other factors which influence the sign of rotation of the ethyl lactate produced, for it has been shown by Senter and Bulle (J., 1912, **101**, 2528) and Senter and Ward (*ibid.*, p. 2534) that during the hydrolysis of sodium α-bromopropionate by water and alkalis two molecules of the salt interact to form an intermediate compound which suffers subsequent hydrolysis. Such a reaction is exceedingly probable in the case of potassium α-p-toluenesulphonoxypropionate.

$$\underset{KO_2C}{\overset{CH_3}{}}>C<\underset{O\cdot SO_2\cdot C_7H_7}{\overset{H}{}} + KO_2C\cdot CH(O\cdot SO_2\cdot C_7H_7)\cdot CH_3 \longrightarrow$$

$$\underset{KO_2C}{\overset{CH_3}{}}>C<\underset{\underset{CH_3}{O\cdot CO\cdot CH\cdot O\cdot SO_2\cdot C_7H_7}}{\overset{H}{}}$$
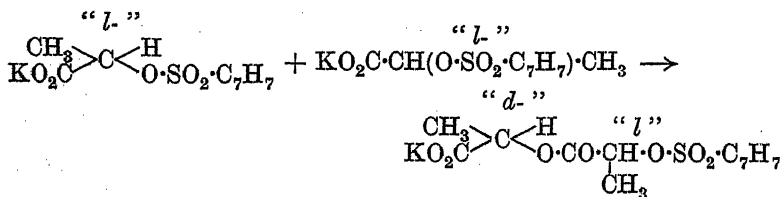
It follows that in this reaction the molecule which loses its p-toluenesulphonoxy-radical may be inverted in configuration, and the subsequent hydrolysis of the complex would then yield a molecule of potassium lactate of the opposite configuration to that of the sulphonic ester. In experiment (3), where the conditions may be considered favourable for such an interaction, the "race-misation" is greater, whilst in experiment (4), where the formation of the potassium salt in small amount was observed and where conditions are ideal for an indirect reaction between two molecules

of this salt, ethyl "*d*"-lactate was obtained of opposite sign of rotation (and configuration) to that of the sulphonate employed.

The formation in experiments 3 and 4 of ethyl α-ethoxypropionate without change of sign taking place is noteworthy. It doubtless arises through the formation of potassium ethoxide by the interaction of potassium hydroxide and the solvent alcohol (compare, *inter alios*, Senter and Wood, J., 1916, **109**, 681), which would give rise to reactions as described on p. 402.

Another possibility, however, must be entertained. From an investigation of the interaction of sodium ethoxide and sodium α-bromopropionate in ethyl-alcoholic and in aqueous ethyl-alcoholic solutions, Senter and Wood (*loc. cit.*) conclude that the intermediate compound $CH_3 \cdot CH(O \cdot CO \cdot CHBrCH_3) \cdot CO_2Na$ is produced by the interaction of two molecules of the salt. This, however, in presence of sodium ethoxide decomposes into sodium α-ethoxypropionate and sodium α-bromopropionate. The formation of sodium α-ethoxypropionate in an analogous manner may occur also in the experiments under discussion, and, since optically active ethyl α-*p*-toluenesulphonoxypropionate was used, may influence in some at present unforeseen manner the sign of rotation of the products.

The Relative Configurations of the Derivatives of Lævorotatory Lactic Acid.

It is suggested that the mode of interaction of the *p*-toluenesulphonyl derivative of ethyl "*d*"-lactate arises directly from one factor, namely, that the "key" atom of the *p*-toluenesulphonoxy-radical is the ester oxygen atom. Under the particularly mild conditions used in the reactions described, the remaining portion of this group, $C_7H_7 \cdot SO_2-$, is a closed and unreactive system; the $-SO_2-$ portion in particular merits this description, since it can be assumed to have that self-sufficing character which it is known to possess in the sulphones.

It is believed that this concentration of reactive power, either actual or potential, in one atom provides a possible explanation of the strong resemblance which exists between the general reactions of *p*-toluenesulphonic esters and organic esters of the halogen acids. The "key" atom in organic halides is the halogen atom itself, but the concentration of reactivity in both classes of compounds in one atom is not of itself sufficient to account for the similarity observed between them. It is suggested, further, that the reactive atom of the halogen compound, as was postulated also in the case of *p*-toluenesulphonic esters, exerts its residual affinity in the direction of the α-hydrogen atom and in this way causes the carbon atom to

become unsaturated. Consider ethyl α-bromopropionate as an example :
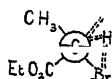
This diagrammatic representation illustrates, on this hypothesis, the condition of an ethyl α-bromopropionate molecule immediately preceding interaction. It is, from a qualitative point of view, exactly the same as that suggested in the case of the *p*-toluene-sulphonate, and it is postulated that it will interact with the salts of the alkalis in an identical manner.
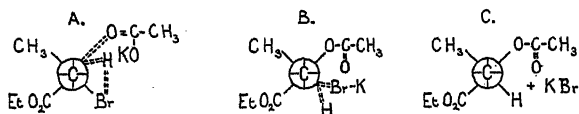
A, B, and C indicate three of the stages in the gradual transition of an ethyl α-bromopropionate molecule into ethyl acetoxypropionate by interaction with potassium acetate. As in the case of the *p*-toluenesulphonic ester, since addition of the potassium acetate must occur on the " quadrant " of the asymmetric carbon atom to which the α-hydrogen atom was attached, inversion of the configuration of the molecule will result. Similarly, a direct reaction can be postulated, passing through a gradual series of changes, of which the three following stages can be visualised—
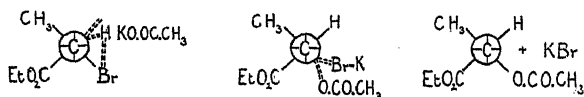
Now it has been shown with a high degree of probability that the *p*-toluenesulphonyl derivative of ethyl " *d* "-lactate reacts with potassium acetate with inversion of 98% of the active molecules participating in the reaction. It is conceivable that the substitution of a bromine atom for an atom of such degree of unsaturation as the ester-oxygen atom of a *p*-toluenesulphonoxy-radical is presumed to possess, may alter the ease with which the compound assumes an " active " condition. It will thus alter the degree of residual affinity of which the asymmetric carbon atom becomes possessed and hence the relative proportions of the direct and the indirect reaction.

It is, however, considered likely that, in a similar reaction under the same experimental conditions, the percentage of molecules of

ethyl α-bromopropionate or of ethyl α-*p*-toluenesulphonoxy-propionate inverted would be of the same order.

Such reactions are those between potassium acetate and the *p*-toluenesulphonyl derivative of ethyl " *d* "-lactate on the one hand, and ethyl α-bromopropionate on the other. Both these esters are soluble in alcohol, and their interaction with potassium acetate leads to the separation from the alcoholic solution of potassium *p*-toluenesulphonate and of potassium bromide, the solubilities of which in alcohol are approximately equal. It is found that lævorotatory ethyl α-bromopropionate yields dextro-rotatory ethyl acetoxypropionate, *i.e.*, of the same sign of rotation as that obtained from ethyl " *l* "-*p*-toluenesulphonoxypropionate :

$$
\begin{array}{ccccc}
\text{" } l \text{ "-} & & \text{" } d \text{ "-} & & \text{" } l \text{ "-} \\
\overset{|}{\underset{|}{\text{CH}_3}} & & \overset{|}{\underset{|}{\text{CH}_3}} & & \overset{|}{\underset{|}{\text{CH}_3}} \\
\text{CH·O·SO}_2\text{·C}_7\text{H}_7 & \xrightarrow[\substack{98\% \\ \text{inverted}}]{\text{CH}_3\text{·CO}_2\text{K}} & \text{CH·O·CO·CH}_3 & \xleftarrow[\substack{75\% \\ \text{inverted *}}]{\text{CH}_3\text{·CO}_2\text{K}} & \text{CHBr} \\
\text{CO}_2\text{Et} & & \text{CO}_2\text{Et} & & \text{CO}_2\text{Et}
\end{array}
$$
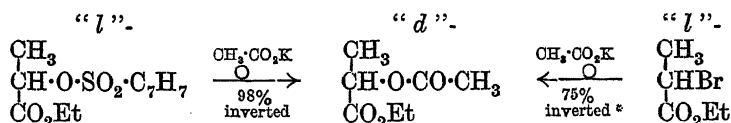
* In the 25% loss in rotatory power is included the loss which may occur during the preparation of the ethyl " *l* "-bromopropionate.

According to this suggestion, it follows that ethyl " *l* "-α-bromo-propionate has the same configuration as the *p*-toluenesulphonyl derivative of ethyl " *l* "-lactate and consequently as dextrorotatory lactic acid. Assuming this conclusion to be correct and incorporating certain results obtained by other workers, the reactions of the derivatives of lactic acid can be represented by the following scheme :
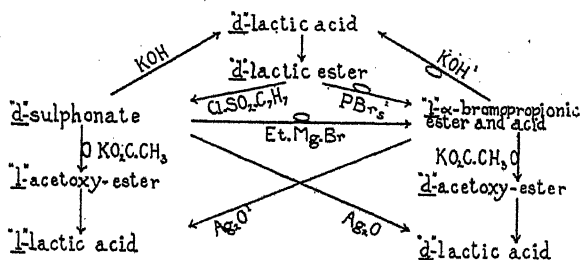
[1] Fischer, *Ber.*, 1907, **40**, 489.   [2] Walker, *J.*, 1895, **67**, 914.

This scheme suggests that the action of magnesium ethyl bromide on the sulphonic ester is an indirect reaction, accompanied by inversion of configuration. This is in agreement with the view that the reactions of Grignard reagents are preceded by addition, and in the present instance this may be regarded as occurring at the asymmetric carbon atom when the sulphonic ester is in its " active " condition.

The *p*-toluenesulphonyl group itself, when associated with an

aromatic nucleus, has been shown to be inert towards Grignard reagents (Ferns and Lapworth, *loc. cit.*).

That sulphonic esters are hydrolysed by caustic potash without inversion of configuration whilst the hydrolysis of α-bromopropionic acid by the same reagent results in configurative change, is doubtless due to the ability of the sulphonic esters to break at the *O—S* linking (p. 404). α-Bromopropionic acid can suffer hydrolysis only between its bromine and asymmetric carbon atoms, and hence every molecule which suffers hydrolysis can undergo inversion of configuration if the conditions are favourable. It must be remembered, also, that Senter and others have conclusively proved that during such hydrolysis interaction occurs between two molecules of the potassium salt of the acid. Should this result in inversion of configuration of one of the molecules of each pair which react, then, if such interaction is considerable, it may determine the sign of rotation of the ultimate product.

Gadamer (*Chem. Ztg.*, 1910, **34**, 1004; 1912, **36**, 1327) has suggested that the action of silver oxide on α-bromopropionic acid is attended with inversion of configuration, but his conception of the reaction suggests the possibility of profound racemisation such as is not found experimentally. Biilmann (*Annalen*, 1911, **388**, 338) is of the opinion that the action of silver ions on α-bromopropionic acid is unaccompanied by change of configuration, a conclusion in agreement with the above scheme, and also with the possible mode of interaction of organic halides suggested herein.

That caustic potash and phosphorus pentabromide may cause inversion of configuration of the compounds with which they react are conclusions previously expressed by Armstrong (J., 1896, **69**, 1399) and by Frankland (J., 1913, **103**, 713) after a comprehensive survey of the experimental data then in existence.

They are in direct opposition, however, to those of Clough (J., 1918, **113**, 526), whose conclusions are based on the assumption that the rotatory powers of compounds, which possess similar constitutions and the same configuration, would be modified in a regular manner by such influences as the following—temperature, solution, introduction of substituents—in each case with as wide a variation as is experimentally available. Whilst his collection of data relating to series of hydroxy-acids, amino-acids, and halogenated acids is in each separate case so varied and extensive as to fulfil the postulate that a comparison should be made over a wide range of external conditions, yet the data by which the relative configurations of the three groups of acids are fixed are, perhaps, insufficient for definite conclusions to be drawn.

The application of the conclusions of Clough to the data given in

this communication demands that *p*-toluenesulphonyl derivatives should be organic compounds of an almost unique type, since they alone would be deemed capable of forming derivatives such as ethoxy-, phenoxy-, bromo-, iodo-, chloro-, acetoxy-, and benzoyloxy-, accompanied by configurative change of the molecule. The reasons for considering this view improbable are given earlier in this paper.

Further, all the suggestions advanced must not be considered applicable, without modification, to acids which have a phenyl group directly attached to the asymmetric carbon atom, since the work of McKenzie, Clough, and others has shown effectively that the behaviour of such acids may differ from that of acids of purely aliphatic character.

The Configurational Relationships of Dextrorotatory α-p-Toluene-sulphonoxypropionic Acid, Lævorotatory Lactic Acid, and their Esters and Amides.

The opportunity was taken to augment the existing data concerning the rotatory powers of derivatives of lactic acid, and to study the effect of temperature, concentration, and the presence of inorganic salts on the rotatory powers of the compounds prepared, since Clough (*loc. cit.*) finds that a change in the external conditions alters the optical rotatory power of a hydroxy-acid in the opposite direction to the alteration produced by the same change in the rotatory powers of its derivatives obtained by replacing the hydrogen atom of the hydroxyl group by another grouping. As an example, the presence of sodium bromide lowers the rotatory power of a methyl-alcoholic solution of dextrorotatory ethyl tartrate, whereas it increases the rotatory power of a similar solution of diacetyl-tartaric acid. Further, Patterson and Forsyth (*J.*, 1913, **103**, 2263) have shown that, whereas the rotation of dextrorotatory methyl lactate in the homogeneous condition is perceptibly increased by a rise in temperature, the dextrorotatory power of methyl acetoxypropionate is thereby slightly decreased. From a study of certain optically active acids and amides of the sugar series, Hudson (*J. Amer. Chem. Soc.*, 1918, **40**, 813) has postulated that all hydroxy-acids which give dextrorotatory amides and hydrazides have the same configuration as the " *d* "-series of acids, *i.e.*, as lævorotatory lactic acid.

When these general principles are applied as in Table I, it will be seen that the conclusion previously stated, that dextrorotatory ethyl α-*p*-toluenesulphonoxypropionate has the same configuration as dextrorotatory ethyl lactate, is completely confirmed.

It was suggested by Wood, Such, and Scarf (*J.*, 1923, **123**, 600) that the complex rotatory dispersion of the esters of lactic acid

P*

TABLE I.

	Lactic acid.	Acetoxy-propionic acid.	p-Toluene-sulphonoxy-propionic acid.
Sign of rotation of the acid.	Negative.	Positive.	Positive.
Sign of rotation of the ethyl ester.	Positive.	Positive.	Positive.
Effect of sodium bromide on the rotation of the acid dissolved in methyl alcohol.	Decreased.	Increased.	Increased.
Effect of rise of temperature on the rotation of the ethyl ester.	Increases the dextro-rotation.	Small decrease in dextrorotation.	Very small decrease in dextrorotation.
The character of the optical dispersive power of the ethyl ester.	Complex.	(Not determined.)	Simple.
Sign of rotation of the amide.	Positive.*	—	Positive.

* Freudenberg, Brauns, and Siegel, *Ber.*, 1923, **56**, [*B*], 193.

is due (*a*) to their persistent low rotatory powers, (*b*) to the influence of the hydroxyl group attached to the asymmetric carbon atom. The rotatory power of ethyl " *d* "-α-*p*-toluenesulphonoxy-propionate was determined over a large range of temperature and for light of several wave-lengths. Under the experimental conditions tried, it exhibited simple rotatory dispersion in marked contrast to the complex rotatory dispersive power shown by ethyl " *d* "-lactate. It is remarkable that this complexity of rotatory dispersion of ethyl " *d* "-lactate should disappear when the *p*-toluenesulphonyl group is substituted for the hydrogen atom of the hydroxyl group attached to the asymmetric carbon atom.

EXPERIMENTAL.

The " *d* "-lactic ester used in this work was obtained by resolving *dl*-lactic acid by means of the morphine salt (Patterson, J., 1913, **103**, 2263), and subsequent esterification. Several methods have been described for the preparation of ethyl lactate, but, owing to its solubility in water and to the great ease with which it undergoes hydrolysis, especially in presence of traces of alkali, its preparation in a state of purity is rendered somewhat tedious and difficult. The recorded rotatory powers of ethyl " *d* "-lactate vary within wide limits, a result which has been shown by Purdie and Williamson (J., 1896, **69**, 818) to be due to the simultaneous formation, during the silver-salt esterification process, of ethyl α-ethoxypropionate, which has almost the same boiling point as ethyl lactate. Sodium lactate has now been easily converted into pure ethyl lactate by

means of ethyl p-toluenesulphonate in yields of over 80% of the theoretical, without the formation of by-products.

Ethyl " d "-lactate was prepared as follows : The aqueous solution of ammonium " d "-lactate obtained by the decomposition of moist morphine " d "-lactate (418 g.) was mixed with sodium carbonate crystals (140 g.) and evaporated to a thick syrup of sodium " d "-lactate, which was extracted with hot absolute alcohol (300 c.c.). The hot extract was heated with ethyl p-toluene-sulphonate (200 g.) under reflux for 3 hours, cooled, and mixed with anhydrous ether (300 c.c.). After removal of the abundant precipitate of sodium p-toluenesulphonate and of the solvents, a further quantity of anhydrous ether was added to the residue to precipitate the remaining sodium p-toluenesulphonate.

After removal of the ether, the residue was twice distilled, when 80 g. of pure ethyl " d "-lactate were obtained, b. p. 50°/10 mm., $d_4^{23°}$ 1·0345, $n_{5896}^{18°}$ 1·4157, $n_{5461}^{18°}$ 1·4176. It showed $\alpha_D^{23°} + 5·84°$ ($l = 50$ mm.), whence $[\alpha]_D^{23°} + 11·29°$, a value which is in excellent agreement with that obtained by Wood, Such, and Scarf (J., 1923, **123**, 600); these authors prepared the ester from zinc ammonium " d "-lactate by Purdie and Williamson's method (*loc. cit.*).
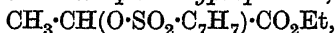
Ethyl " d "-α-p-*toluenesulphonoxypropionate*,
$$CH_3·CH(O·SO_2·C_7H_7)·CO_2Et,$$
is readily prepared in good yield by adding p-toluenesulphonyl chloride (42 g.) to an ice-cold mixture of ethyl " d "-lactate (26 g.) and pyridine (26 g.). After 12 hours, water is added, and the mixture worked up in the usual way. The sulphonic ester distils without decomposition at 164—166°/0·5 mm.; it is a viscous, heavy, highly refractive, colourless oil which could not be induced to solidify.

0·2862 required 0·0835 of sodium hydroxide for complete hydro-lysis. Calc. 0·0842.

The determinations of density and of optical rotatory power are given in Table II.

The sulphonic ester was not distilled prior to its use in the following experiments. The very small amount of low-boiling material which the crude ester contained was, however, removed by gentle heating in a vacuum.

If the solution of ethyl " d "-lactate in pyridine was allowed to become warm during the addition of the sulphonyl chloride, or if the mixture of pyridine hydrochloride and " d "-α-p-toluenesulphon-oxypropionate produced remained in contact for longer than 12 hours, this substance of low boiling point was obtained in larger quantities. On investigation, it proved to be lævorotatory ethyl α-chloropropionate. It had b. p. 41°/14 mm., $d_4^{20°}$ 1·072, $n_D^{18°}$ 1·4166, and $\alpha_D^{17°} - 15·04°$.

Similarly from lævorotatory ethyl lactate, $[\alpha]_D^{20°}$ — 7·26°, dextrorotatory chloropropionic ester, $\alpha_D^{17°}$ + 10·10°, was obtained (compare p. 413).

Ethyl α-p-toluenesulphonoxypropionate can also be prepared by the interaction of the sulphonyl chloride and the potassium derivative of ethyl lactate,

$$CH_3 \cdot CH(OK) \cdot CO_2Et + C_7H_7 \cdot SO_2Cl =$$
$$CH_3 \cdot CH(O \cdot SO_2 \cdot C_7H_7) \cdot CO_2Et + KCl,$$
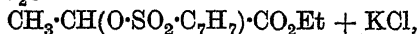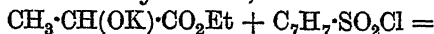
but in this case the yields are small, and, in addition, the product is completely racemised.

" d "-α-p-*Toluenesulphonoxypropionic acid* was readily prepared by shaking together ethyl " d "-α-p-toluenesulphonoxypropionate (10 g.), baryta (7 g.), and water (200 c.c.). After ½ hour, the clear solution was acidified and the precipitated oil extracted with ether. After removal of the solvent, the residue set to a crystalline mass, m. p. 108°. Yield 93%. When crystallised from a mixture of benzene and light petroleum, the acid softened at 105° and melted at 108°.

0·2940 required 0·0963 of sodium hydroxide for complete hydrolysis, the theoretical amount being 0·0964.

0·6480 required 0·1063 of sodium hydroxide for neutralisation; equiv. = 241.   Calc. for $C_{10}H_{12}O_5S$, 244.

The determinations of rotatory power are given in Table II.

" d "-α-p-*Toluenesulphonoxypropionamide* was obtained by vigorously shaking together for 1 hour a mixture of ethyl d-α-p-toluenesulphonoxypropionate (4 g.) and ammonium hydroxide (d 0·88; 50 c.c.) and filtering off the snow-white crystals. The amide crystallises from hot water in fine, silky needles, m. p. 105—106° 'Found : N = 5·6. $C_{10}H_{13}O_4NS$ requires N = 5·76%).

Reaction between Ethyl " d "-α-p-Toluenesulphonoxypropionate and the Potassium Salts of Carboxylic Acids.

*Ethyl-" d "-α-Benzoyloxypropionate.**—A mixture of ethyl " d "-p-toluenesulphonoxypropionate (10 g.), potassium benzoate (12 g.), and absolute alcohol (50 c.c.) was heated under reflux for 12 hours. The benzoyl derivative, obtained by pouring the product into water and extracting the oil with ether (yield almost quantitative), had · b. p. 153°/12 mm., $d_{4°}^{20°}$ 1·112, $n_{5461}^{13°}$ 1·5006, $\alpha_D^{20°}$ + 13·65° (l = 50 mm.), whence $[\alpha]_D^{20°}$ 24·56°.

Ethyl " l "-α-benzoyloxypropionate, prepared, for purposes of comparison, by the interaction of benzoyl chloride and ethyl " d ".

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* This ester and the others described were fractionated until subsequent redistillation left their rotatory powers unaltered.

lactate, distilled at 149°/10 mm. and had $d_4^{20°}$ 1·114, $n_D^{15°}$ 1·4973, $n_{5461}^{15°}$ 1·5010, $\alpha_D^{20°}$ − 13·70° ($l = 50$ mm.), whence $[\alpha]_D^{20°}$ − 24·60°.

Ethyl " l "-α-Phenylacetoxypropionate.—A mixture of ethyl " d "-*p*-toluenesulphonoxypropionate (5 g.), freshly-fused potassium phenylacetate (19 g.), and absolute alcohol (50 c.c.) was heated under reflux for 12 hours and worked up as previously described. The ester distilled at 160—162°/14 mm. and had $d_4^{19°}$ 1·1001, $n_D^{16°}$ 1·4920, $\alpha_D^{19°}$ − 20·69° ($l = 50$ mm.), whence $[\alpha]_D^{19°}$ − 37·61°.

Ethyl " d "-α-phenylacetoxypropionate was prepared for purposes of comparison by the interaction of phenylacetyl chloride and ethyl " d "-lactate. It distilled at 161—162°/13 mm. and had $d_4^{22°}$ 1·1006, $n_D^{19°}$ 1·4904, $\alpha_D^{22°}$ + 21·21° ($l = 50$ mm.), whence $[\alpha]_D^{22°}$ + 38·54°.

Ethyl " l "-α-acetoxypropionate was prepared by heating under reflux for 12 hours a mixture of ethyl " d "-α-*p*-toluenesulphonoxypropionate (15 g.), potassium acetate (11 g.), and absolute alcohol (50 c.c.). The product (yield 80%) distilled at 71—72°/10 mm. and had $d_4^{18°}$ 1·0442, $n_D^{19°}$ 1·4096, $\alpha_D^{18°}$ − 24·87° ($l = 50$ mm.), whence $[\alpha]_D^{18°}$ − 47·63°.

Ethyl " d "-α-acetoxypropionate, prepared by the action of acetyl chloride on ethyl " d "-lactate, had b. p. 73—74°/11 mm., $n_D^{19°}$ 1·4096, $\alpha_D^{22°}$ 27·00° ($l = 50$ mm.), whence $[\alpha]_D^{22°}$ − 51·54°.

Reaction between Potassium Acetate and Dextrorotatory Ethyl α-Bromopropionate in Ethyl-alcoholic Solution.—The dextrorotatory ethyl α-bromopropionate required was prepared by Walker's method (J., 1895, **67**, 914) from partly active ethyl lactate having $\alpha_D^{20°}$ − 6·94°.

Dextrorotatory ethyl α-bromopropionate, $\alpha_D^{20°}$ − 20·6° (3 g.), and potassium acetate (3 g.) were dissolved in 20 c.c. of absolute ethyl alcohol. After heating under reflux for 6 hours, the product, ethyl α-acetoxypropionate, was isolated in the usual way. It had b. p. 75°/15 mm., $n_D^{17°}$ 1·4110, and $\alpha_D^{18°}$ − 6·03° ($l = 25$ mm.), and hence $[\alpha]_D^{18°}$ − 23·1°.

Reaction between the p-*Toluenesulphonate of Ethyl Lactate and Alkali Halides in Ethyl-alcoholic Solution.*

(*a*) *With Lithium Chloride.*—The lævorotatory sulphonate (15 g.), prepared from lævorotatory ethyl lactate, $[\alpha]_D^{20°}$ − 7·26°, and 6·6 g. of lithium chloride were dissolved in 50 c.c. of ethyl alcohol and heated under reflux for 12 hours. The mixture was poured into water, and the oil which separated was isolated in the usual manner. Ethyl α-chloropropionate (6·5 g.) was obtained, b. p. 48—49°/18 mm., $d_4^{25°}$ 1·0720, $n_D^{20°}$ 1·4166, and $[\alpha]_D^{25°}$ + 2·82°.

(*b*) *With Sodium Bromide.*—The " d "-sulphonate (15 g.) and

15 g. of crystalline sodium bromide were used and treated as under (a). Ethyl α-bromopropionate (9·4 g.) was obtained, b. p. 55—56°/10 mm., $d_4^{19°}$ 1·3841, $n_D^{19°}$ 1·4450, and $\alpha_D^{16°}$ — 0·58°.

(c) *With Potassium Iodide.*—The " *d* "-sulphonate (15 g.) and 18 g. of potassium iodide were used and treated as in (a) and (b). Ethyl α-iodopropionate (13 g.) was obtained, b. p. 74—75°/16 mm., $d_4^{20°}$ 1·6637, $n_D^{20°}$ 1·4985, and $[\alpha]_D^{20°}$ — 0·12°.

Reaction between the p-*Toluenesulphonate of Partly Active Ethyl Lactate* ($\alpha_D^{26°}$ — 6·94°) *and Grignard Reagents.*

(a) *With Magnesium Ethyl Bromide.*—To the ice-cold reagent prepared from 5·5 g. of ethyl bromide, 100 c.c. of ether, and 1·2 g. of magnesium, the lævorotatory sulphonate (12 g.) in 50 c.c. of ether was slowly added, the reaction being vigorous; and the mixture was heated under reflux for 1 hour. Water was then added slowly, followed by dilute hydrochloric acid, and the ethereal solution was washed first with water and then with dilute sodium carbonate solution. After drying with anhydrous sodium sulphate, the ether was removed and the dextrorotatory ethyl α-bromo-propionate distilled. It weighed 4 g. and had b. p. 63°/20 mm., $n_D^{20°}$ 1·4407, $\alpha_D^{20°}$ + 4·45° ($l = 25$ mm.), $[\alpha]_D^{20°}$ + 17·80°.

(b) *With Magnesium Phenyl Bromide.*—The procedure described above was closely followed. From 12 g. of lævorotatory sulphonate were obtained 5 g. of dextrorotatory ethyl α-bromopropionate, b. p. 60°/15 mm., $d_4^{20°}$ 1·387, $\alpha_D^{20°}$ + 3·96° ($l = 25$ mm.), and hence $[\alpha]_D^{20°}$ + 15·84°.

(c) *With Magnesium Ethoxy Iodide.*—8 G. of methyl iodide in 100 c.c. of ether were treated with 1·3 g. of magnesium, after the dissolution of which, 2·6 g. of ethyl alcohol in 50 c.c. of ether were slowly added. The lævorotatory sulphonate (15 g. in 50 c.c. of ether) was then added, the mixture heated under reflux for 1 hour, and the product isolated as described above. The dextrorotatory ethyl α-iodopropionate obtained (yield 60%) had b. p. 77°/18 mm., $d_4^{22°}$ 1·6463, $\alpha_D^{22°}$ + 1·88°.

Hydrolysis of Lævorotatory Ethyl α-p-*Toluenesulphonoxypropionate.* —Portions of the *p*-toluenesulphonyl derivative of partly active ethyl lactate, $\alpha_D^{20°}$ — 7·26°, were used in the following experiments :—

(a) *With sodium hydroxide.* The lævorotatory sulphonate (15 g.) and sodium hydroxide (4·5 g.) were shaken in cold water (70 c.c.) for 2 hours. The solution was made acid to phenolphthalein with sulphuric acid, and evaporated to dryness. The solid residue of dextrorotatory sodium lactate was esterified, using ethyl *p*-toluene-sulphonate. Lævorotatory ethyl lactate (3 g.) was finally obtained with $\alpha_D^{20°}$ — 5·20°.

(b) *With potassium hydroxide.* The sulphonate (12 g.), potassium hydroxide (4 g.), and ethyl alcohol (50 c.c.) were heated under reflux for 2 hours. The solution was evaporated to dryness, and the potassium salts esterified as before. The mixture (3 g.) of ethyl α-ethoxy- and α-hydroxy-propionates obtained had α_D^{20} — 11·60°. It was warmed for 1 hour with acetyl chloride and redistilled. 2 G. of lævorotatory ethyl α-ethoxypropionate, b. p. 52°/15 mm., $\alpha_D^{20°}$ — 14·0°, and 1 g. of lævorotatory ethyl α-acetoxypropionate, b. p. 73°/15 mm., $\alpha_D^{20°}$ — 19·56°, were obtained.

Lævorotatory ethyl α-acetoxypropionate prepared from the same sample of lævorotatory ethyl lactate had $\alpha_D^{20°}$ — 32·0°.

(c) *With silver oxide.* The ester was first converted into the corresponding acid (see p. 412). The lævorotatory α-p-toluenesulphonoxypropionic acid thus obtained (13 g.) was warmed for 2 hours with silver oxide (from 20 g. of silver nitrate), suspended in 200 c.c. of water. The silver oxide, after dissolution, was reprecipitated by potassium hydroxide, the solution filtered, and the filtrate neutralised and evaporated to dryness. The potassium lactate thus obtained was esterified with ethyl p-toluenesulphonate and yielded lævorotatory ethyl lactate (2 g.), $\alpha_D^{22°}$ — 5·84°.

Reaction between Alkyl Oxides and Ethyl " d "-α-p-Toluenesulphon-oxypropionate.—(a) *With potassium phenoxide.* By the interaction of ethyl " d "-α-p-toluenesulphonoxypropionate (15 g.) and potassium phenoxide (6·4 g.) in 50 c.c. of absolute alcohol, 8 g. of ethyl " l "-α-phenoxypropionate were obtained which distilled at 125—127°/16 mm., and had $d_4^{22°}$ 1·0620, $n_D^{21°}$ 1·4946, $\alpha_D^{23°}$ — 7·73° ($l = 50$ mm.), whence $[\alpha]_D^{23°}$ — 14·56°.

(b) *With sodium ethoxide.* The ethyl α-ethoxypropionate obtained was inactive.

Reaction between the Sodium Derivative of Ethyl " d "-Lactate and Ethyl p-Toluenesulphonate.—To powdered sodium (1·4 g.), suspended in benzene, were added 7 g. of ethyl " d "-lactate in 20 c.c. of the same solvent. After dissolution of the sodium, a solution of 12 g. of ethyl p-toluenesulphonate in 20 c.c. of benzene was added, and the mixture heated under reflux for 12 hours. After cooling and addition of 100 c.c. of ether, the solution was filtered. The solvents were removed from the filtrate, and the residue distilled. The ethyl α-ethoxypropionate thus obtained had b. p. 55—57°/16 mm., and $\alpha_D^{31°}$ + 1·94°.

Reaction between the p-Toluenesulphonate of Lævorotatory Ethyl Lactate and Ethyl Alcohol in presence of Potassium Carbonate.

A mixture of lævorotatory sulphonate (15 g., prepared from lævorotatory ethyl lactate having $\alpha_D^{20°}$ — 6·94°), potassium carbonate

(7·6 g.), and ethyl alcohol (50 c.c.) was heated under reflux for 12 hours. The mixture was then treated as previously described and the final product after esterification had b. p. 54—55°/16 mm., $d_4^{21°}$ 0·9959, and $[\alpha]_D^{25°}$ — 5·46°.

The high density seemed to indicate the presence of ethyl lactate. The product was therefore warmed for 1 hour with an equal volume of acetyl chloride and then redistilled. Dextrorotatory ethyl α-acetoxypropionate, b. p. 78°/17 mm., α_D 1·00° ($l = 25$ mm.) (whence $\alpha_D^{21°}$ + 4·00°), and 1 g. of lævorotatory ethyl α-ethoxypropionate, b. p. 57°/17 mm., $\alpha_D^{21°}$ — 8·72, were obtained.

Lævorotatory ethyl α-acetoxypropionate, prepared from the same sample of lævorotatory ethyl lactate used for the preparation of the lævorotatory sulphonate, had $\alpha_D^{21°}$ — 30·30°.

Physical Measurements.

Densities were determined in a pyknometer of about 1·5 c.c. capacity. Polarimetric measurements were made using as sources of monochromatic light the sodium and lithium flames and the enclosed mercury arc.

The rotatory powers of ethyl "d"-α-p-toluenesulphonoxypropionate were observed in a jacketed tube ($l = 50$ mm.), round which hot oil was circulated for the readings at higher temperatures.

Owing to the highly refractive and viscous nature of this compound, the observed values are accurate only to 0·2°.

Ethyl "d"-α-p-Toluenesulphonoxypropionate.

Temp. ...	20·5°	40°	60°	80°	100°	120°	140°
$d_4^{t°}$	1·2025	1·1845	1·1662	1·1464	1·1296	1·1119	1·0893
	$n_{5896}^{16·5°}$ 1·5011				$n_{5461}^{16·5°}$ 1·5040		

Rotatory Power.

λ_{6708}·· +20·5° at 21°; 18·8° at 40°; 17·6° at 60°; 16·10° at 82°; 15·1° at 101°; 13·9° at 121°.

λ_{5893}· 27·3° at 21°; 25·2° at 40°; 22·6° at 60°; 21·5° at 82°; 20·2° at 101°; 18·6° at 121°.

λ_{5790}· 28·6° at 21°; 25·5° at 40°; 23·0° at 60°; 22·0° at 82°; 22·6° at 101°; 18·9° at 121°.

λ_{5461}· 32·2° at 21°; 29·2° at 40°; 27·3° at 60°; 24·9° at 82°; 23·4° at 101°; 21·8° at 121°.

λ_{4359}· 56·1° at 21°; 50·6° at 40°; 46·2° at 60°; 42·3° at 82°; 39·6° at 101°; 36·3° at 121°.

The following figures are obtained from the smoothed curves drawn through the above values :

TABLE II.

$t°$.	$d_{4°}^{t°}$.	λ 6708.	λ 5893.	λ 5790.	λ 5461.	λ 4359.	a_{4359}/a_{5461}.
20°	1·2010	+34·3°	45·6°	47·6°	53·9°	93·9°	1·74
40	1·1845	31·9	42·6	43·3	50·0	85·7	1·73
60	1·1662	30·2	40·2	40·3	46·5	79·2	1·70
80	1·1464	28·3	38·0	38·2	43·8	74·3	1·69
100	1·1296	26·9	35·9	36·2	41·7	69·9	1·68
120	1·1119	25·2	33·7	34·3	39·5	65·7	1·66

TABLE III.

Determination of Rotatory Power of (A) " d "-α-p-Toluenesulphon-oxypropionic Acid in Various Solvents.

Length of Observation Tube = 200 mm. $T = 25°$.

Solvent.	G. of solute in 100 c.c. of solution.	$a_\lambda^{25°}$.					$[a]_\lambda^{25°}$.				
		6708.	5893.	5790.	5461.	4359.	6708.	5893.	5790.	5461.	4359.
Ethyl alcohol ...	4·95	+2·79°	+3·58°	+3·66°	+4·12°	+6·95°	+28·2°	+36·2°	+37·0°	+41·6°	+70·2°
Benzene ...	2·35	1·29	1·42	1·51	1·74	2·94	27·5	30·2	32·2	37·1	62·7
Chloroform	4·97	3·37	4·21	4·74	4·85	8·31	33·7	41·3	47·7	48·8	83·6
Methyl alcohol ...	4·96	3·44	4·58	4·83	5·73	9·28	34·7	46·1	48·7	57·8	92·6
N-Sodium bromide in methyl alcohol ...	5·03	3·70	5·08	—	6·23	10·58	38·8	50·5	—	61·9	104·8

(B) " d "-α-p-*Toluenesulphonoxypropionamide.*

Ethyl alcohol ...	5·25	+2·66	+3·40	+3·78	+4·24	+7·50	+22·4	+32·3	+36·0	+40·4	+71·5

BATTERSEA POLYTECHNIC,
LONDON, S.W. 11.

LXII.—*The Relative Rates of Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part I. Aliphatic Ethylenic Derivatives.*

By S. V. LEBEDEV, G. G. KOBLIANSKY, and A. O. YAKUBCHIK.

THIS communication deals with the results of the first part of an investigation which we have undertaken in order to examine how far the rate at which hydrogenation proceeds is controlled

by the substituent groups in proximity to the ethylenic linking, and also in what manner the progress of the action is altered when mixtures of similar or different types of unsaturated compounds are submitted to hydrogenation.

From this point of view we have examined (i) aliphatic ethylenic compounds, (ii) alicyclic unsaturated compounds, (iii) conjugated, non-conjugated, and allenic diethylenic compounds, and (iv) unsaturated compounds containing nitrogenous substituents or containing heterocylic systems.

The most important result of the experiments now described— those dealing with open-chain ethylenic unsaturation—is that it has been found possible to indicate the constitution of an unsaturated compound by hydrogenating it in admixture with another ethylenic derivative of known constitution.

The rate of absorption of hydrogen by unsaturated compounds in presence of platinum or palladium black was first studied by Fokin (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 419; 1907, **39**, 607; 1908, **40**, 276), who concluded that the action was unimolecular and dependent on the diminishing concentration of the unsaturated substance. In many of his experiments, however, the logarithmic nature of the change is evident in the final stages only, and a careful examination shows that the critical part of most of his curves forms a straight line.

In the meantime, other observers, including Vavon (*Compt. rend.*, 1911, **152**, 1675), Willstätter (*Ber.*, 1912, **45**, 1471), S. V. Lebedev (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1002), Armstrong and Hilditch (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137; 1920, [*A*], **98**, 27), and Salkind (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 191), have pointed out that hydrogen is absorbed at a constant rate by unsaturated liquids in presence of a metal catalyst.

We are not concerned here to discuss the mechanism of what we regard as a very complex process, further than to affirm that the observed rate of absorption of hydrogen is a linear function of the time, and to postulate that the action proceeds by the formation of an unstable intermediate product (of the nature of an adsorption compound) between catalyst and unsaturated molecule, with the further restriction that only molecules which are adsorbed by the catalyst undergo hydrogenation.

Whilst, however, unsaturated compounds frequently display a uniform velocity of hydrogen absorption throughout nearly the whole course of the process of hydrogenation, certain cases have been brought forward in which a compound containing more than one ethylenic linking shows two well-defined rates of hydrogenation, corresponding with the disappearance of first one and then another

of the unsaturated groups. Examples which may be mentioned are dipentene (Vavon, *loc. cit.*); linolein, linolenin, etc., amongst other unsaturated glycerides (Armstrong and Hilditch, *loc. cit.*); and the dimeric phenylbutadiene examined by one of us (*loc. cit.*).

On the other hand, an unpublished observation by Lebedev and Yakubchik has been made that in the case of diethylenic compounds the individual unsaturated residues may be hydrogenated either at the same, or at different rates.

It will be seen later that the same phenomena are also characteristic of *mixtures of mono-ethylenic compounds :* Each hydrogenation may proceed independently of the other, with the result that a mean constant rate of absorption of hydrogen is observed, or the compounds may be hydrogenated consecutively, one being almost unattacked until the other has disappeared. In other words, the catalyst (platinum black in our experiments) may possess a selective affinity either for different parts of the same unsaturated molecule or, in the other case, for differently constituted, unsaturated molecules.

Experimental Method and Interpretation of Results.

The catalyst employed throughout was platinum black prepared by the method of Loew as modified by Willstätter (*loc. cit.*).

The hydrogenations were conducted at atmospheric temperature and pressure in solutions of the various compounds in absolute alcohol, employing approximately $0·01$ mol. of the compounds in about 10—15 c.c. of alcohol, with an amount of catalyst present varying from $0·05$ to $0·3$ gram, or, in a few cases, even greater amounts.

In general, the effect of doubling the concentration of catalyst in a given case was to increase the rate of absorption of hydrogen by about 50%.

The hydrogen used was prepared by electrolysis of a solution of caustic soda, the gas being passed over heated copper and then dried through a column of soda-lime and calcium chloride.

The hydrogenations were carried out in a horizontal glass vessel fitted with two stoppered necks, one for the admission of hydrogen, the other for filling purposes. When studying volatile compounds, we used a special filling pipette attached to the latter neck by means of a ground-glass joint, so that it was possible to ensure admission of the compound in an atmosphere of hydrogen without loss by evaporation.

The hydrogenation vessel, connected to the hydrogen burettes by a flexible tube, was shaken horizontally at the rate of 250

oscillations per minute, by an eccentric gearing of the usual type coupled to an electric motor.

During the absorption of hydrogen, readings were, as a rule, taken at intervals of half a minute; with high rates of absorption, the accuracy of the measurements was about $\pm$ 0·25 c.c., and for lower rates, $\pm$ 0·1 c.c. Rates of absorption higher than 20 c.c. per 0·5 minute were observed only in a few cases.

In previous work of this kind it has been usual to represent the data graphically by plotting the total absorption of hydrogen against the time from the commencement of the experiment; we have adopted the alternative of plotting increments of absorption against equal ($\frac{1}{2}$-min.) increments of time. This method appears more advantageous in that it depicts with maximum sharpness any alteration in the rate of hydrogenation, and—in the application of our results to determining the nature of an unsaturated compound—the points at which abrupt changes in rate of absorption occur are those of most importance to our immediate purpose.

Consequently, whereas the "linear curves" of other workers have shown a series of connected lines commencing at the origin and altering more or less sharply from a greater to a lesser slope, in our graphs a constant rate of hydrogen absorption is represented by a straight line parallel to the axis of abscissæ, and changes in the rate are marked by a pronounced drop to a horizontal at a lower level.

The enhanced clearness of this mode of illustration is shown in Fig. 9, curves 2 and 2', which depict the rate of absorption of hydrogen by a mixture of styrene and oleic acid. The "break" in each curve is marked by a dash, and it will be seen that the method employed throughout this paper (curve 2) shows much more clearly the point at which the change in absorption-rate occurs than the more usual type of curve (2').

In the figures, time intervals of 0·5 min. are given as abscissæ and the number of c.c. of hydrogen absorbed per 0·5 min. as ordinates. For the curve 2' in Fig. 9 only, each division of the axis of ordinates corresponds to 10 c.c. of absorbed hydrogen; this is indicated by the figures 50 and 100 on the right of the axis.

Since the curves illustrate completely the data on which we base our conclusions, it has not been thought necessary to tabulate the increments of absorption in detail, and therefore in the corresponding tables there will be found merely a summary of the remaining data pertaining to each experiment.

In each table the compounds examined are numbered, the correspondingly numbered curves in the figures showing the increment–absorption-rates for a given compound or mixture.

The tables also show the amounts of platinum-black catalyst, alcohol (solvent), and compound employed, together with the calculated volume of hydrogen required for saturation and the volume actually absorbed, at $t°$ and the pressure of experiment.

The experimental results which we are able to put forward include :

(i) Hydrogenation of single ethylenic compounds—monosubstituted, symmetrically or non-symmetrically disubstituted, tri- and tetra-substituted.

(ii) Hydrogenation of mixtures of ethylenic compounds of a similar degree of substitution.

(iii) Hydrogenation of mixtures of ethylenic compounds of different degrees of substitution.

(iv) Illustration of the application of the varying rates of hydrogenation of a mixture of ethylenic compounds to the determination of the nature of one of the unsaturated compounds or to quantitative analysis of a mixture of known compounds.

The following general results of this part of the investigation may be noted :

(a) Monosubstituted ethylenic derivatives possess the highest rate of absorption of the various classes examined, and also the rate of absorption is constant throughout by far the greater part of the reaction.

The peculiar increase in reaction velocity toward the end of the process in the case of allyl alcohol (curve 1) is due to some factor which has not been made clear, and moreover, it is not always to be observed with the compound.

Two diethylenic derivatives also are included in the table :

The curve for diallyl is practically identical with that for *iso*-propylethylene (No. 5), so that it may be concluded that each ethylenic linking is attacked as though, in this case, the other were not present.

The curve for allyl cinnamate in the first phase of the process, on the other hand, is almost the same as that for allyl alcohol (No. 1) ; but the concentration of catalyst in the former instance is only half that in the latter, so that for equal concentrations the absorption-rate for allyl cinnamate would be of the same form as, but about 50% more rapid than, that for allyl alcohol.

This is an example of the effect produced on the rate of hydrogenation of the monosubstituted ethylene by the presence in the molecule of a further double linking of a different (symmetrically disubstituted) type ; we shall return to this later in dealing with the hydrogenation of mixtures of ethylenic compounds.

(b) Symmetrically disubstituted ethylenic compounds also are

TABLE I (corresponding with Fig. 1).

Hydrogenation of Single Ethylenic Compounds.

(a) *Monosubstituted ethylenic derivatives,* $R·CH:CH_2$.

No.	Compound.	Formula.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.). Calc.	Found.	t°.	Press. (mm. of Hg).
1	Allyl alcohol.	$CH_2:CH·CH_2·OH$	0·3146	0·2	15	136	136	13	760
2	Eugenol.	$CH_2:CH·CH_2·C_6H_3(OH)·OMe$	1·6529	0·2	13	233	230	15	770
3	Styrene.	$CH_2:CHPh$	0·6485	0·2	40	125	123	19	770
4	Allylacetone.	$CH_2:CH·CH_2·CH_2·COMe$	0·9801	0·2	10	231	228	19	760
5	isoPropylethylene.	$CH_2:CH·CHMe_2$	0·7700	0·2	10	260	257	14	760
6	Diallyl.	$CH_2:CH·CH_2·CH_2·CH:CH_2$	0·5000	0·2	7	281	284	16	770
7*	Allyl cinnamate.	$CHPh:CH·CO·O·CH_2·CH:CH_2$	0·8291	0·1	9	105		12	760

* The curve (7) is not shown in Fig. 1. It is similar to curve 2.

TABLE II (corresponding with Fig. 2).

(b) *Symmetrically disubstituted ethylenic derivatives,* $R'·CH:CHR''$.

No.	Compound.	Formula.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.). Calc.	Found.	t°.	Press. (mm. of Hg).
1	Oleic acid.	$CH_3·[CH_2]_7·CH:CH·[CH_2]_7·CO_2H$	2·7475	0·2	90	233	258	15	750
2	Crotonic acid.	$CHMe:CH·CO_2H$	0·9016	0·2	10	250	254	14	750
3	Anethole.	$MeO·C_6H_4·CH:CHMe$	0·8862	0·2	14	144	146	17	760
4	Cinnamyl alcohol.	$CHPh:CH·CH_2·OH$	1·0653	0·2	13	184	185	14	770
5	Methyl cinnamate.	$CHPh:CH·CO_2Me$	0·7900	0·1	10	117	*	22	755
6	Maleic acid.	$CO_2H·CH:CH·CO_2H$	0·7844	0·1	15	98	100	20	750
7	Stilbene.	$CHPh:CHPh$	0·6000	0·1	70	*	*	19	770

* The rate of absorption was very slow in these cases and the results are not shown in the graph.

as-*Dimethylcarboxysuccinic Acid* (VI).—The preceding ester (25 g.) was boiled with 110 c.c. of aqueous potassium hydroxide (3 parts KOH : 4 parts H_2O) for 24 hours, another 20 g. of potassium hydroxide were then added, and the boiling was continued until no more ammonia was given off (about 50 hours). The cooled, cautiously acidified liquid on extraction with much ether gave an acid (yield almost theoretical), m. p. 164—166° (decomp.); 166—167° (decomp.) after crystallisation from ether-chloroform (Found : C = 44·4; H = 5·5; M = 192. $C_7H_{10}O_6$ requires C = 44·2; H = 5·3%; M = 190). The acid forms minute prisms which are very soluble in water, moderately so in ether, and sparingly soluble in chloroform. On heating to 170° in a sulphuric acid bath, the acid is smoothly converted into as-dimethylsuccinic acid and carbon dioxide.

Ethyl as-*Dimethylcarboxysuccinate* (III).—The silver salt, prepared from the tribasic acid (9·5 g.), carbonate-free sodium hydroxide (3 mols.; prepared from sodium), and excess of concentrated silver nitrate solution, was washed with water, alcohol, and ether, and thoroughly dried. A suspension of the dry salt (52 g.) in 500 c.c. of dry ether was gently heated with 60 g. of ethyl iodide on the steam-bath for 3·5 hours, the silver iodide filtered off after 2 days and thoroughly washed with dry ether. From the combined filtrate and washings a residue was obtained which, twice distilled, gave 16 g. of the ester, b. p. 158—165°/22 mm. (Found : C = 56·5; H = 7·9. $C_{13}H_{22}O_6$ requires C = 56·9; H = 8·0%). On hydrolysis with hydrochloric acid as-dimethylsuccinic acid was produced.

Action of Sodium Ethoxide on Ethyl as-*Dimethylcarboxysuccinate*, (a) *at* 78°.—The ester (13·6 g.) was heated for 19 hours with alcoholic sodium ethoxide (1·15 g. of sodium; 14 g. of alcohol), the mixture poured into water, extracted with ether, and the ethereal solution dried and evaporated. The residue was hydrolysed with boiling 20% hydrochloric acid. On cooling, a considerable quantity of pure as-dimethylsuccinic acid crystallised, and the mother-liquors, on evaporating by fractions and finally to dryness, yielded successive crops of the same pure acid unaccompanied by any α-methylglutaric acid.

(b) *At* 100°.—In a similar experiment, carried out in a closed vessel at 100° for 170 hours, a mixture of neutral and acid esters was obtained. These were separated in the usual way with ether and sodium carbonate and hydrolysed by hydrochloric acid to the dibasic acids, which were fractionally crystallised in the manner previously described, yielding, in addition to much as-dimethyl-succinic acid, more soluble and more fusible fractions consisting essentially of α-methylglutaric acid, but in quantity insufficient for

hydrogenated at a constant rate throughout about half of the action, but at a somewhat slower speed than the monosubstituted class, and, in the cases where the substituent is an aromatic or acidic group, at a very definitely reduced rate.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

O.c. of hydrogen absorbed in 0·5 minute.
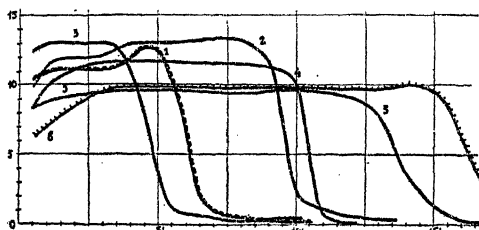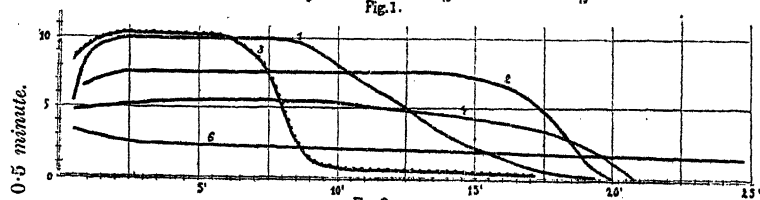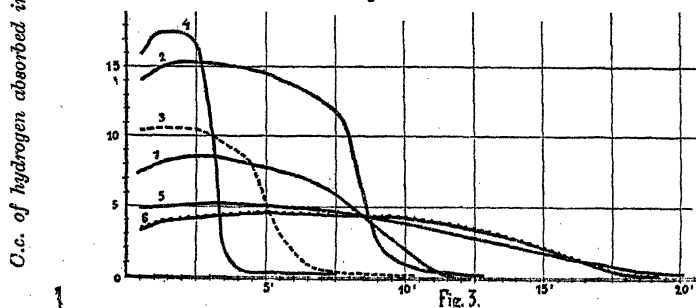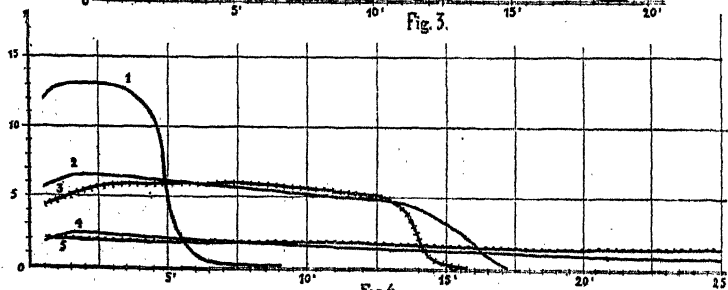
Time in 0·5 *minute.*

The rate of absorption during the second half of the action gradually declines.

(c) With non-symmetrically disubstituted ethylenic compounds the presence of a phenyl or carboxylic residue causes a lower general

rate of absorption. It is also notable that the reaction velocity declines more or less consistently from the commencement except in the cases of camphene and methylene*cyclo*hexane, where a uniform rate of absorption characterises the earlier part of the process; it is to be noted that both these compounds contain the double bond attached externally to an alicyclic carbon ring-system.

(*d*) Of the three trisubstituted ethylenic compounds examined, two show an approximately linear or very slowly falling type of absorption of hydrogen, whilst the third, mesityl oxide, containing a conjugated system of an ethylenic and a carbonyl group, is marked by an uncommonly high rate of absorption during the hydrogenation of the ethylenic linking.

The tetrasubstituted compounds examined exhibit a very low, but approximately constant, rate of hydrogenation.

Summing up all the results, the highest rates of hydrogenation are shown by the monosubstituted compounds and the lowest by the tetrasubstituted, the other types falling in between; the presence of negative substituents seems to induce an abnormally slow velocity, whilst conjugation with alicyclic or carbonyl residue tends to accelerate the rate of reaction.

Mono- and tetra-substituted derivatives absorb hydrogen at an approximately constant rate throughout nearly the whole of the process, trisubstituted ethylenes also are nearly " linear " in their rates of absorption, but with both classes of disubstituted derivatives the constancy of rate is only maintained at most for a period of the whole action.

Hydrogenation of Mixtures of Ethylenic Compounds.

The remarkable mutual influence of unsaturated compounds present in a mixture on their individual rates of hydrogenation appears to us, as stated on p. 418, to be the most important result of our investigation. We were led to observe this effect in consequence of an attempt which we made to render our data more comparable by adding a proportion of a definite ethylenic derivative in the hope that we might be able to detect a characteristic absorption rate for this compound and thus reduce all the rates of absorption to a definite standard. We had hoped in this way to eliminate errors due to the erratic retarding effect of certain influences which are exceedingly difficult to detect, such as :

The slight variation in activity of different preparations of platinum black ;

the alteration in activity with age of the same preparation of the catalyst ;

TABLE V (Figs. 5—8).

Hydrogenation of mixtures of ethylenic compounds of a similar degree of substitution.

Monosubstituted ethylenic derivatives (Fig. 5).

No.	Compounds.	Mean rate of hydrogenation (c.c. per 0.5 min.).		Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.).		$t°$.	Press. (mm. of Hg).
		Individually.	Mixed.				Calc.	Found.		
1	{ Eugenol. Allyl alcohol.	9 7.5	12	0.5455 0.2373	0.1	10	80 } 180 100	177.5	20	760
2	{ Eugenol. Styrene.	9 10	18	0.7318 0.4495	0.1	15	107 } 212 105	210	21	760
3	{ Eugenol. isoPropylethylene.	13 99.5	15	0.8110 0.5000	0.2	13	115	292	14	765
4	{ Allylacetone. isoPropylethylene.	17 14	16.5	0.9775 0.4000	0.3	13	233	366	14	775

Symmetrically disubstituted ethylenic derivatives (Fig. 6).

No.	Compounds.	Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Calc.	Found.	$t°$.	Press.
1	{ Oleic acid. Crotonic acid.	7.5 6.5	8	0.8950 0.2492	0.1	30	77 } 154.5 77.5	152	20	755
2	{ Anethole. Crotonic acid.	10 8.5	9.5	0.6510 0.8380	0.2	12	108 } 344 236	347	14	740
3	{ Anethole. Cinnamyl alcohol.	14 8	9.25	1.4924 0.7159	0.4	10	234 } 359 125	362	15	770
4	{ Anethole. Oleic acid.	10 10	13	1.3394 1.4563	0.2	70	210 } 330 120	348	15	770

the risk of depreciating the catalyst by exposure to air during transference to the hydrogenation apparatus;

the presence of impurities, especially oxidation products, in the substance which is to be hydrogenated.

We found, however, that the rate of absorption of hydrogen by a binary mixture of ethylenic derivatives was directly dependent on the constitution of the components, and examination of a large number of such mixtures led us to the following generalisations, which are illustrated by the absorption–time curves of the examples given in the tables which follow :

1. In a mixture of two similarly substituted ethylenic compounds the components are hydrogenated concurrently and the resulting graph is either a smooth curve or a straight line.

2. In a mixture of two dissimilarly substituted ethylenic compounds the components are hydrogenated, broadly speaking, consecutively and the resulting graph is a discontinuous curve.

On our primary assumption (p. 418) that only those molecules which are adsorbed by the catalyst can suffer addition of hydrogen, this involves the consequences that metallic catalysts must possess exceedingly selective powers of adsorption, and that the degree of adsorption is approximately the same for similarly substituted compounds and quite different for. those of differing orders of substitution.

The corresponding graphs are shown in Figs. 5—8, and a dash has been inserted at the point on each curve at which, had the process been one of selective or consecutive hydrogenation, a break-point should have occurred.   In point of fact no such break occurs in any instance, and all the curves retain the smooth character of those of the components of the mixtures employed.

The general conclusions to be drawn are that in the case of binary mixtures of similarly substituted ethylenic compounds :

(1) The general type of the absorption–time graphs is the same as that of the components, according to the manner of substitution of the latter (compare pp. 421—425).

(2) Most frequently the rate of absorption is fairly close to the mean of those of the individual components; in other words, selective hydrogenation is not operating and both compounds are absorbing hydrogen concurrently.

(3) If one of the components has an unusually high linear rate of absorption, such as camphene or mesityl oxide, the rate of hydrogenation of the binary mixture of similarly substituted compounds frequently tends to approach this relatively high rate, rather than the true mean; and the resulting graph is similar to that for the

more active substance, but is still a smooth curve or linear graph
throughout its course.
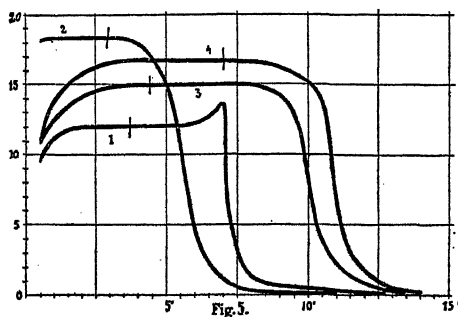
Fig. 5.
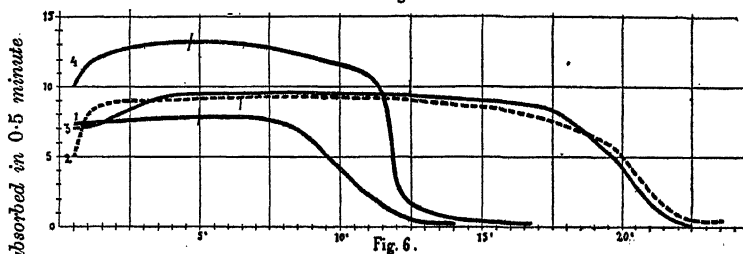
Fig. 6.
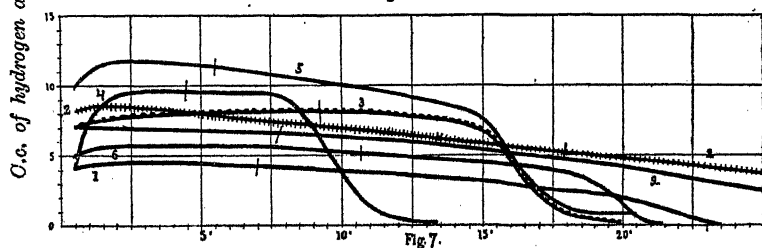
Fig. 7.

Fig. 8.

Time in 0·5 minute.
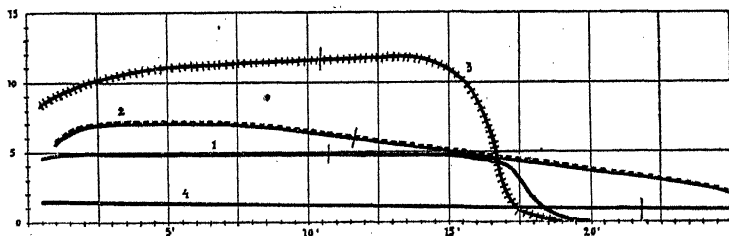
O.c. of hydrogen absorbed in 0·5 minute.

(4) The continuity of the hydrogenation curves and the complete
absence of break-points are the most characteristic features of this
type of mixture.

TABLE VI (Figs. 9—17).

Hydrogenation of mixtures of ethylenic compounds of different degrees of substitution.

Monosubstituted + symmetrically disubstituted ethylenes (Fig. 9).

No.	Compounds.	Mean absorption rate (c.c. per 0.5 min.). Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.). Calc.	Found.	t°.	Press. (mm. of Hg)
1	{ Allyl alcohol. / Crotonic acid.	7 / 6·5	8·5 / 1	0·3544 / 0·2761	0·1	10	148 / 77 }225	242	22	760
2	{ Styrene. / Oleic acid.	10 / 7·5	10 / 8·5	0·2660 / 0·7807	0·1	40	61 / 64 }125	140	20	760
3	{ Eugenol. / Oleic acid.	9·5 / 7·5	18 / 8·5	0·8952 / 1·0710	0·1	40	131 / 90 }221	226	20	760
4	{ Eugenol. / Anethole.	13 / 10	20·5 / 11	0·8260 / 1·6029	0·2	40	120 / 260 }380	385	12	740

Monosubstituted + non-symmetrically disubstituted ethylenes (Fig. 10).

No.	Compounds.	Mean absorption rate (c.c. per 0.5 min.). Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.). Calc.	Found.	t°.	Press. (mm. of Hg)
1	{ Allyl alcohol. / Diphenylethylene.	11 / 4	17·5 / 1	0·3302 / 0·7467	0·2	14	138 / 102 }240	250	20	750
2*	{ Eugenol. / Diphenylethylene.	13 / 4	23 / 1·5	0·8997 / 0·3125	0·2	14	130·5 / 42 }172·5	180	19	755
3	{ Eugenol. / Itaconic acid.	13 / 4	12·5 / 5·5	0·9992 / 0·5125	0·2	14	145·5 / 94·5 }240	243	19	765
4	{ Allyl alcohol. / Methyl-*tert.*-butylethylene.	11 / 15	9·5 / 2	0·3923 / 1·2778	0·2	13	160 / 305 }465	454	15	760
5	{ Eugenol. / Methyl-*tert.*-butylethylene.	13 / 15	12 / 5·5	1·6758 / 0·4621	0·2	13	243 / 111 }354	350	13	760
6	{ Allyl alcohol. / Camphene,	10 / 8	10 / 3	0·3147 / 1·0720	0·15	14	130 / 188 }318	314	19	760

* Curve 2, Fig. 10, is not shown. It is similar to curve 1,

TABLE VI (continued).

Monosubstituted + trisubstituted ethylenes (Fig. 11).

No.	Compounds.	Mean absorption rate (c.c. per 0.5 min.), Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.), Calc.	Found.	t°.	Press. (mm. of Hg)
1	{ isoPropylethylene.	9.5	11.5	0.3763	0.2	15	126 } 303	268	13	760
	{ Trimethylethylene.	6.5	6.75	0.4380			177 }			
2	{ Allyl alcohol.	7	10	0.2710	0.1	15	114 } 168	173	23	755
	{ Mesityl oxide.	9	2	0.2205			54 }			
3	{ Eugenol.	13	21	1.6165	0.2	13	233 } 394	394	15	760
	{ Mesityl oxide.	13	10	0.6690			161 }			
4	{ isoPropylethylene.	9.5	15.25	0.5510	0.2	13	182 } 406	409	14	775
	{ Methylheptenone.	5.5	9	1.2205			224 }			

Monosubstituted + tetrasubstituted ethylenes (Fig. 12).

No.	Compounds.	Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Calc.	Found.	t°.	Press.
1	{ Allyl alcohol.	11	9	0.3336	0.2	10	190 } 260	*	19	750
	{ Tetramethylethylene.	1	0.5	0.2300			70 }			
2	{ Eugenol.	13	11.5	1.5480	0.2	12	220 } 383	*	15	740
	{ Tetramethylethylene.	1	1	0.5590			163 }			

Symmetrically + non-symmetrically disubstituted ethylenes (Fig. 13).

No.	Compounds.	Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Calc.	Found.	t°.	Press.
1	{ Oleic acid.	10	6.5	1.5170	0.2	50	130 } 229	240	19	765
	{ Itaconic acid.	4	4	0.5372			99 }			
2	{ Crotonic acid.	12	10	0.5483	0.3	13	149 } 378	382	13	760
	{ Itaconic acid.	6	7.5	1.2650			229 }			
3	{ Anethole.	10	14.25	0.7930	0.2	11	127 } 381	363	17	760
	{ Methyl-tert.-butylethylene.	15	11.5	1.0530			254 }			
4	{ Crotonic acid.	11.5	16.5	0.8685	0.35	13	241 } 371	365	14	750
	{ Methyl-tert.-butylethylene.	18.5	17	0.5330			130 }			
5	{ Cinnamyl alcohol.	8	6.5	0.9198	0.3	13	163 } 239	242	16	760
	{ Methyl-tert.-butylethylene.	18	7.25	0.3142			76 }			

* The rate of absorption was very slow in the second phase of the process and the experiments were not finished.

TABLE VI (continued).

Symmetrically disubstituted + trisubstituted ethylenes (Fig. 14).

No.	Compounds.	Mean absorption rate (c.c. per 0.5 min.)		Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Hydrogen absorbed (c.c.).		t°.	Press. (mm. of Hg).
		Individually.	Mixed.				Calc.	Found.		
1	{ Crotonic acid.	8·5	9·5	0·9158	0·2	13	250 } 374	380	14	760
	Mesityl oxide.	13	8·5	0·5198			124 }			
2	{ Cinnamyl alcohol.	7	7·25	0·4555	0·3	13	81 } 269	271	15	750
	Trimethylethylene.	8	5·25	0·5475			188 }			
3	{ Anethole.	12	7·5	1·5129	0·3	12	246 } 401·5	408	14	760
	Mesityl oxide.	15	10·25	0·6404			155·5 }			
4	{ Anethole.	10	8·5	0·8055	0·2	13	128 } 317	310	13	760
	Methylheptenone.	6	8	1·0164			189 }			

Non-symmetrically disubstituted + trisubstituted ethylenes (Fig. 15).

No.	Compounds.	Individually.	Mixed.	Amount (g.).	Platinum (g.).	Alcohol (c.c.).	Calc.	Found.	t°.	Press. (mm. of Hg).
1	{ Diphenylethylene.	5	2	0·5111	0·2	14	71 } 185	189	19	760
	Mesityl oxide.	13	9·5	0·4680			114 }			
2	{ Methyl-tert.-butylethylene.	15	12·5	0·6066	0·2	13	177 } 387	384	14	750
	Mesityl oxide.	13	13·5	0·9846			210 }			
3	{ Methylphenylethylene.	11	7·5	0·7978	0·3	12	102 } 342	345·5	13	765
	Methylheptenone.	7·25	5	1·2977			240 }			
4	{ Camphene.	10	10·5	0·6820	0·2	15	135 } 323	319	13	750
	Mesityl oxide.	13	9·75	0·7743			188 }			
5*	{ Methyl-tert.-butylethylene.	15	9	0·8650	0·2	13	206 } 374	373	14	760
	Trimethylethylene.	6·5	8	0·5000			168 }			
6*	{ Camphene.	10	11	0·7487	0·2	13	131 } 306	300	14	750
	Trimethylethylene.	6·5	10·25	0·5814			175 }			

* Curves 5 and 6 (Fig. 15) are not shown, being similar to 4.

TABLE VI (continued).

Symmetrically disubstituted + tetrasubstituted ethylenes (Fig. 16).

No.	Compounds.	Mean absorption rate (c.c. for 0·5 min.).		Amount (g.)	Platinum (g.)	Alcohol (c.c.).	Hydrogen absorbed (c.c.).		t°.	Press. (mm. of Hg).
		Individually.	Mixed.				Calc.	Found.		
1	{Crotonic acid.	7·5	11	0·4354	0·2	14	121}192	170	19	750
	{Tetramethylethylene.	1	?	0·2506			71}			
2*	{Cinnamyl alcohol.	5·5	3·25	0·5862	0·2	13	104}193	?	14	750
	{Tetramethylethylene.	1	0·5	0·2955			89}			

Non-symmetrically disubstituted + tetrasubstituted ethylenes (Fig. 17).

No.	Compounds.	Individually.	Mixed.	Amount (g.)	Platinum (g.)	Alcohol (c.c.).	Calc.	Found.	t°.	Press. (mm. of Hg).
1*	{Itaconic acid.	4	4	0·4632	0·2	14	85}178	170	17	760
	{Tetramethylethylene.	1	2·5	0·3270			93}			
2	{Methyl-tert.-butylethylene.	15	14	0·8456	0·2	13	204}320	315	15	755
	{Tetramethylethylene.	1	2	0·4103			116}			

Trisubstituted + tetrasubstituted ethylenes (Fig. 17).

No.	Compounds.	Individually.	Mixed.	Amount (g.)	Platinum (g.)	Alcohol (c.c.).	Calc.	Found.	t°.	Press. (mm. of Hg).
3	{Mesityl oxide.	13	10·75	0·6155	0·2	9	150}214	219	19	755
	{Tetramethylethylene.	1	2	0·2260			64}			
4	{Trimethylethylene.	6·5	11·25	0·8345	0·2	13	278}337	340	14	760
	{Tetramethylethylene.	1	1	0·2095			59}			

* For curve 2 (Fig. 16) and curve 1 (Fig. 17) we marked off the volumes of hydrogen absorbed in 1 minute.

So much is this the case, that if hydrogenation of a binary mixture of ethylenic compounds results in an absorption–time curve which is either linear or continuously falling without any abrupt break, we are able to predict with considerable confidence that both unsaturated compounds are similarly substituted with regard to the carbon atoms concerned in the ethylenic linking.

Hydrogenation of Ethylenic Compounds of Different Degrees of Substitution.

About forty binary mixtures of mono-, di-, tri-, or tetra-substituted ethylenes have been examined in which the components belong to different types of substitution, and the results, which are as consistent among themselves as the foregoing, display a very notable contrast, all the curves indicating that the hydrogenations proceeded consecutively or selectively, a pronounced discontinuity in the graph appearing at, or very close to, the point at which the hydrogen absorbable by the less-heavily substituted component had in fact disappeared.

These data are summarised in Table VI; the corresponding curves being shown in Figs. 9—17.

A general survey of the data in Table VI leads to the following conclusions :

1. In every case the absorption–time graph is discontinuous, and more or less pronounced breaks occur : the unsaturated compounds are hydrogenated consecutively. (The points at which the compound first attacked would be completely saturated if hydrogenation were completely selective are marked on the graphs by dashes as before, and it will be observed that, in general, there is a close correspondence between these points and the actual places of discontinuity.)

2. In all cases the monosubstituted derivatives are hydrogenated the most readily and the tetrasubstituted ethylenes the most slowly, the other classes falling intermediately.

3. For mixtures of monosubstituted ethylenes with other types of ethylenic compounds, the graphs show very pronounced discontinuities, the two segments being more or less horizontal. The difference in the rates of absorption of hydrogen by the two unsaturated compounds is always marked; usually the monosubstituted compound maintains its characteristic absorption-rate, that of the other compound being sometimes increased above its normal value, and not infrequently markedly diminished.

4. Monosubstituted ethylenes are readily distinguished from the other types by measurements of the rate of hydrogenation in the manner described above.

5. Binary mixtures containing symmetrically or non-symmetric-ally disubstituted or trisubstituted ethylenic compounds show
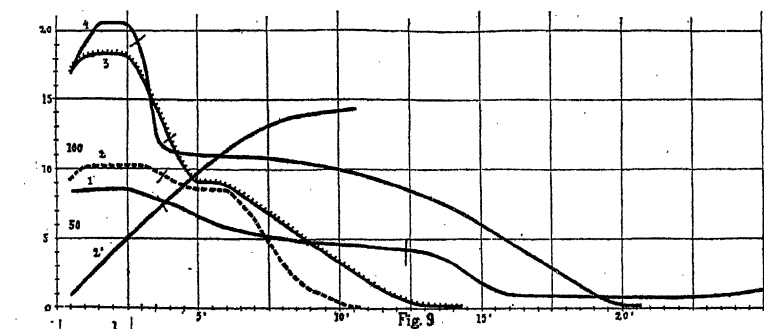
Fig. 9

Fig. 10.

Fig. 11.

Fig. 12.

Time in 0·5 minute.
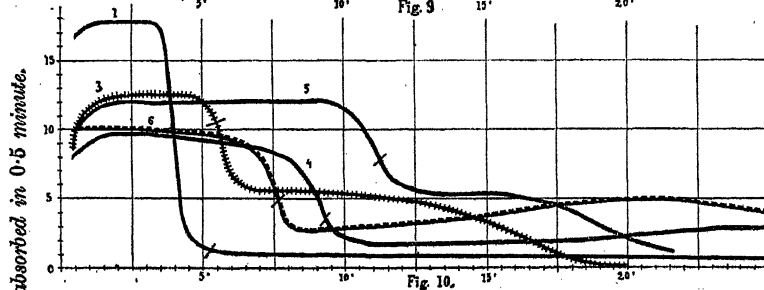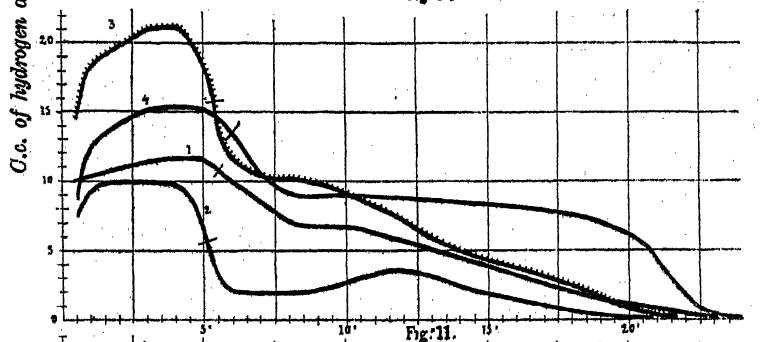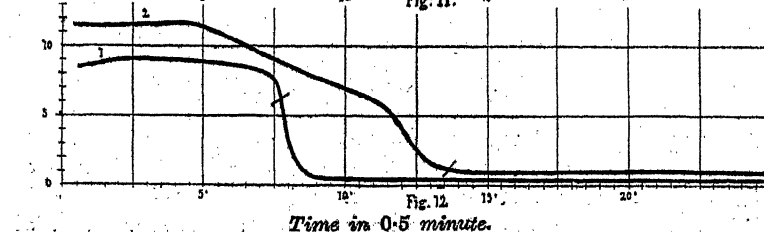
less marked discontinuities, and there is a distinct tendency for the individual absorption-rates to be lowered on the one hand and

raised on the other, so that the absorption-rates of the compounds in admixture are more nearly alike than those of the compounds hydrogenated individually.

Fig. 13.

Fig. 14.

Fig. 15.

Fig. 16.

C·c. of hydrogen absorbed in 0·5 minute.

Time in 0·5 minute.
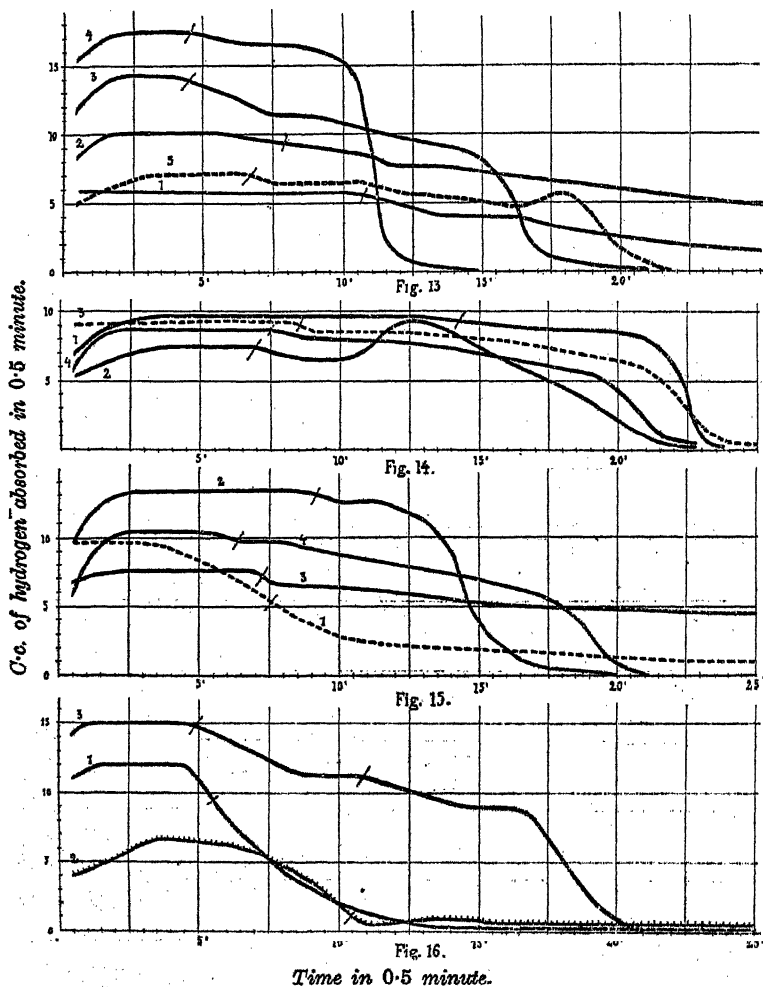
Although we have not encountered such a case, it is evident, from what we have pointed out as to the approximation in rate of hydrogenation of the components, that instances might arise in which the rates of absorption of hydrogen of a binary mixture of di- or tri-substituted ethylenes were the same, although the actual hydrogenation were consecutive. In this case a perfectly smooth

hydrogenation-curve would not necessarily connote concurrent hydrogenation of each unsaturated compound.

6. In binary mixtures of tetrasubstituted ethylenes with the other classes, the individual absorption-rates are altered but little. Owing to the slow rate of hydrogenation of the tetrasubstituted compounds, the difference in the rates of absorption during the two phases of the process is large.
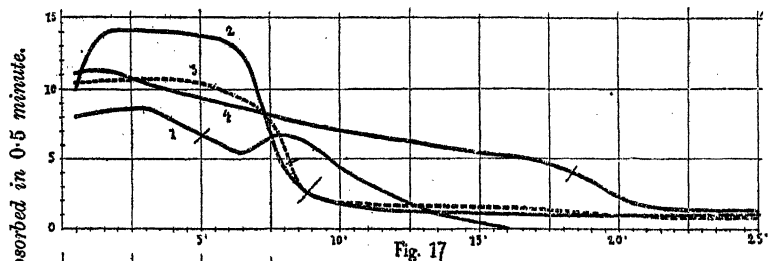
Fig. 17
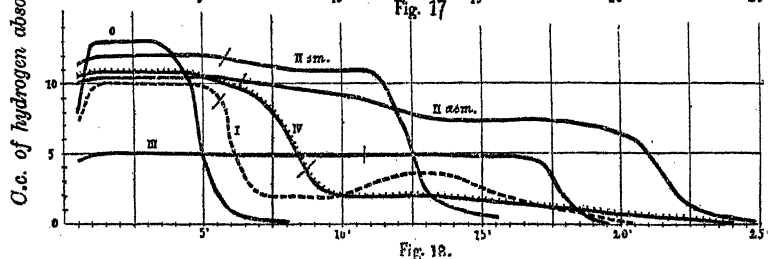
Fig. 18.

Time in 0·5 minute.

Illustrations of the Application of the Foregoing Results to the Determination of the Nature of an Unsaturated Compound, and to Quantitative Analysis of a Mixture of Known Unsaturated Compounds.

Determination of Constitution.—The above generalisations may be utilised to identify the order of substitution of an ethylenic compound by hydrogenating it first alone, and then in binary mixtures with typical compounds of either of the four types of substituted ethylenes.

These five determinations would in general be reduced to three or even two, since in most cases the form of the hydrogenation curve for the individual compound would afford some clue, whilst in most others a certain amount of collateral analytical data may be presupposed which would be of assistance.

As standard typical compounds we recommend the following, which we have selected on the basis of affording suitable rates of

hydrogenation and of being easily procurable and not difficult to obtain in a state of purity.

Monosubstituted :	Allyl alcohol or eugenol.
Symmetrically disubstituted :	Crotonic acid or anethole.
Non-symmetrically disubstituted :	Camphene.
Trisubstituted :	Mesityl oxide or trimethylethylene.
Tetrasubstituted :	Pulegone or tetramethylethylene.

Camphene and mesityl oxide have a tendency to render linear the absorption–time curves of their mixtures with similarly substituted ethylenic compounds, which individually display a steadily declining rate of hydrogenation; this affords a sure indication of the order of substitution in these particular instances.

To illustrate the application of our method, we may assume that we wish to discover the degree of substitution of mesityl oxide. The hydrogenation curves for this compound (o), and for mixtures of the compound with allyl alcohol (i), anethole (ii sm.), methyl-*tert.*-butylethylene (ii asm.), trimethylethylene (iii), and tetramethylethylene (iv) are shown in Fig. 18.

In this particular case (compare p. 425) the results with the individual compound would lead us to suppose it to be monosubstituted, were it not for the very pronounced break in the curve for its mixture with the monosubstituted allyl alcohol. All the other curves also show well-defined discontinuities except number iii, which is remarkably smooth.

From this, the constitution of a trisubstituted ethylene of the general type RCH:CR'R" would be assigned to the compound.

Similarly, if the constitution of methyl-*tert.*-butylethylene were in dispute, the method would render ready assistance. The curve for the pure compound (Fig. 3, curve 2) shows a steadily declining rate of absorption of hydrogen, and suggests that the substance is non-symmetrically disubstituted. This is confirmed at once by the rate of hydrogenation of the substance in admixture with the non-symmetrically disubstituted ethylenic derivative, camphene (Fig. 7, curve 4), when an absolutely smooth curve results.

It will be gathered that monosubstituted compounds (R·CH:CH₂) and tetrasubstituted compounds (RR'C:CR"R''') are those which can be differentiated most readily by observation of rates of hydrogenation. It is more difficult to discriminate between ethylenes of the types RCH:CHR', RR'C:CH₂, and RCH:CR'R", owing to the characteristic differences in their rates of hydrogenation frequently being but small.

Considerable accuracy is then required in determining the rates of absorption per unit of time; this may be assisted by employing a high concentration of catalyst and working with as large a

quantity of material as possible, so that the horizontal positions of the graphs are made as definite as possible.

Quantitative Estimation of the Components of a Mixture.—An approximate estimation of the amounts of the components in a mixture of unsaturated compounds can be made from the hydrogenation curve if allowance is made for the fact, which we have established experimentally, that the end of absorption by one constituent corresponds with a point just beyond where the curve commences to sag from the horizontal.

We have applied our method to the mixture of amylenes obtained by catalytic dehydration of *sec.*-amyl alcohol (fusel oil) in presence of alumina according to the method of Ipatiev. This mixture consists of *iso*propylethylene, *as.*-methylethylethylene, and trimethylethylene.

A typical hydrogenation curve for the mixture is shown in Fig. 16, curve 3, and consists of three more or less horizontal segments. Measurement of the total volume of hydrogen absorbed over each section of the curve gave the following results :

	Expt. 1.	Expt. 2.
*iso*Propylethylene (monosubstituted)	32	31
Methylethylethylene (non-symmetrically disubstituted)	32	32
Trimethylethylene (trisubstituted)	36	37

The figures for experiment 2 were from a separate hydrogenation.

Conclusions.

1. The components of mixtures of ethylenic derivatives of the same type of substitution are hydrogenated concurrently. The curves of hydrogenation of such mixtures have the form of a smooth straight or curved line.

2. The components of mixtures of ethylenic derivatives of different types of substitution are hydrogenated consecutively and selectively. In all cases, monosubstituted derivatives, $R \cdot CH:CH_2$, are attacked preferentially, whilst tetrasubstituted compounds, $RR'C:CR''R'''$, are hydrogenated last of all.

The di- and tri-substituted types, $RCH:CHR'$, $RR'C:CH_2$, and $RR'C:CHR''$, fall intermediately, with less striking differences between them than between this group and either of the preceding.

The hydrogenation curves of mixtures of ethylenic derivatives of varying types of substitution are discontinuous and display definite break-points.

3. It is possible to throw light on the degree of substitution of

an ethylenic compound by observing its rate of hydrogenation (i) in the pure state and (ii) admixed with chosen standard derivatives belonging to one or other of the known types of substitution.

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LXIII.—*The Reactions of Sodium Mono-, Di-, and Tri-sulphides with 1-Chloro-2-nitro-, 1-Chloro-4-nitro-, and 1 : 4-Dichloro-2-nitro-benzene.*

By HERBERT HENRY HODGSON and JAMES HENRY WILSON.

As a preliminary step in an investigation of the conditions of formation of sulphide dyes, the behaviour of sodium mono-, di-, and tri-sulphides with the above chloronitrobenzenes has been examined.

In such reactions, as Blanksma (*Rec. trav. chim.*, 1901, **20**, 141) and others have shown, sodium monosulphide may display at least three kinds of activity, represented by the equations

$$2Na_2S + H_2O + 2O_2 = Na_2S_2O_3 + 2NaOH \text{ (reduction)}$$
$$Na_2S + H_2O \rightleftharpoons NaSH + NaOH \text{ (hydrolysis)}$$
$$2Na_2S + 2H_2O = Na_2S_2 + 2NaOH + 2H \text{ (disulphide formation)}.$$
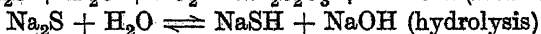
In consequence of this, and the presence of labile chlorine atoms in the organic compounds, the reactions of sodium monosulphide with the chloronitrobenzenes were manifold; moreover, the addition of sodium hydroxide to suppress the hydrolysis of the sulphide produced further complications, and, in the case of 1-chloro-2-nitrobenzene, steric hindrance was yet another factor modifying the course of the reaction.

The reactions of sodium di- and tri-sulphides with the chloronitrobenzenes were comparatively simple, disulphides or mixtures of disulphide and sulphur being produced. In accordance with Blanksma's experience (*loc. cit.*, p. 121), what appear to be two forms of 4 : 4'-dinitrodiphenyl disulphide, m. p. 170° and 180°, respectively, were obtained (compare, however, Zincke and Lenhardt, *Annalen*, 1913, **400**, 1). No nitro-trisulphides were isolated and it seems very probable that Blanksma's 2 : 2'-dinitrodiphenyl trisulphide, m. p. 185°, and tetrasulphide, m. p. 160°, were mixtures of the disulphide and sulphur.

4 : 4'-Diaminodiphenyl trisulphide has been isolated, and its identity as a chemical individual established. This is a definite step in the elucidation of the structure of the polythiozone complexes which are generally believed to occur in the sulphide dyes.

EXPERIMENTAL.

For convenience' sake, the products obtained in the experiments tabulated below are denoted by numerals: I, 1-chloro-2-nitrobenzene; II, 1-chloro-4-nitrobenzene; III, 1 : 4-dichloro-2-nitrobenzene; IV_o, 2-chloroaniline; IV_p, 4-chloroaniline; V_o and V_p, 2 : 2'- and 4 : 4'-dinitrodiphenyl sulphide; VI_o and VI_p, 2'-nitro-2-amino- and 4'-nitro-4-amino-diphenyl sulphide; VII_o and VII_p, 2- and 4-nitrophenyl mercaptans; $VIII_o$ and $VIII_p$, 2 : 2'- and 4 : 4'-dinitrodiphenyl disulphides; IX_o and IX_p, 2- and 4-aminophenyl mercaptans; X_o and X_p, 2 : 2'- and 4 : 4'-diaminodiphenyl disulphides; XI, 4 : 4'-diaminodiphenyl trisulphide.

Reaction of Sodium Sulphide, $Na_2S,9H_2O$.

With 1-Chloro-2-nitrobenzene (I).

Sub- stance (g.).	$Na_2S,9H_2O$ (g.).	NaOH (g.).	Water (c.c.).	Duration of boiling (hrs.).	Product.
			In alcoholic solution.		
6	5	—	—	21	I, 3 g.; IV_o, 0·6 g.; V_o, 1·5 g.
			In aqueous suspension.		
6	5	—	400	12	I, 3 g.
,,	20	—	—	12—20 (fusion)	V_o almost entirely.
,,	,,	—	100	12—20 (boiling)	$V_o : VII_o = 2 : 1$.
,,	,,	—	200	,,	VII_o almost entirely.
,,	24	—	400	,,	IV_o (= 12% of I taken).
3	12	—	50	12 hrs. in sealed tube at 200°.	IV_o, V_o, VII_o (about 1 g. of each).
6	36	12	100	12	VI_o and 32% of IV_o.

With 1-Chloro-4-nitrobenzene (II).

			In alcoholic solution.		
6	5	—	—	6	40% unchanged. IV_p, 17%; V_p, 83%.
6	36	—	—	26	17% unchanged. V_p, 20%.
			In aqueous solution.		
6	5	—	200	3	1 g. unchanged. V_p and a little VI_p.
10	40	—	200	12	IV_p, 2½%; VI_p, 4—5 g. (isolated as hydrochloride); X_p, 2—3 g.
10	40	7	200	12	IV_p, 1%; $VI_p : X_p = 1·7 : 1$.

With 1 : 4-dichloro-2-nitrobenzene (III).

			In alcoholic solution (30 c.c.).		
6	5	—	—	6	1 g. unchanged. 4 : 4'-Dichloro-2 : 2'-dinitrodiphenyl sulphide.*

The same result was obtained in aqueous suspension, but the rate of reaction was slower.

* M. p. 145—146°. Found: Cl = 20·2; S = 9·5. Calc., Cl = 20·57; S = 9·2%.

Ω*

When 1 mol. each of 1-chloro-2-nitrobenzene and 1-chloro-3-nitrobenzene in aqueous suspension were boiled with 4—6 mols. of sodium sulphide, quantitative yields of 3-chloroaniline and 2-aminophenyl mercaptan (isolated as $2:2'$-diaminodiphenyl disulphide) were obtained.

1-Chloro-2-nitrobenzene (3 g.), suspended in water (50 c.c.), was treated with potassium hydrosulphide (made from 3 g. of caustic potash in 20 c.c. of water). The mixture was boiled for 8 hours, re-saturated with hydrogen sulphide, and boiled again for 2 hours. The products were V_o (1 g.), IX_o (0·6 g.; isolated as X_o), and IV_o (0·4 g.). Replacement was therefore more pronounced than that occurring with sodium sulphide. In alcoholic solution, the products were IV_o (1·1 g.) and IX_o (1 g.; isolated as X_o); the non-formation of V_o indicates that the potassium hydrosulphide behaved as such during the reaction.

Reaction of Sodium Disulphide.

Preparation.—The disulphide was prepared by dissolving equivalent quantities of crystallised sodium sulphide and sulphur in the minimum of water.

With 1-chloro-2-nitrobenzene (I).

Substance (g.).	Na_2S_2 (g.).	NaOH (g.).	Water (c.c.).	Duration of boiling (hrs.).	Product.
\multicolumn{6}{l}{*In alcoholic solution.*}					
2 mols.	1 mol.	—	—	1—2	$VIII_o$ almost quant.
,,	6 mols.	—	—	6—8	90% VII_o (isolated as X_o).
\multicolumn{6}{l}{*In aqueous suspension.*}					
6 g.	5·7 g.	—	100	4	4 g. unchanged. IV_o, 0·2 g. Remainder was mercaptan.
,,	30	—	200	24	IX_o (isol. as X_o); IV_o, 0·3 g.; trace of $2:2'$-diaminodiphenyl sulphide, m. p. 85°.
,,	13·5	12	100	12	VI_o almost quant.; IV_o, 7%; trace of IX_o and the sulphide, m. p. 85°.

With 1-chloro-4-nitrobenzene (II).

\multicolumn{6}{l}{*In alcoholic solution* (30 c.c.).}					
,,	5·7	—	—	4	$VIII_p$ (both forms), 5 g.
,,	23	—	—	4	IV_p, 8·9% (similar result with 1-iodo-4-nitrobenzene).
\multicolumn{6}{l}{*In aqueous suspension.*}					
5	34	—	150	40	XI and X_p (isol. after oxidation with air; yield quant.); IV_p, 2%.
5	$\begin{cases} 30 \text{ g. } Na_2S,9H_2O \\ 2 \text{ g. } S \end{cases}$		150	40	X_p quant.
6	5·4		150	12	2·5 g. unchanged. $VIII_p$ and VI_p main product; IV_p, 1%.

With 1 : 4-dichloro-2-nitrobenzene (III).

Sub-stance (g.).	Na_2S_2. (g.).	NaOH (g.).	Water (c.c.).	Duration of boiling (hrs.).	Product.
In alcoholic solution (30 c.c.).					
6	5·7	—	—	½	4 : 4'-Dichloro-2 : 2'-dinitrodiphenyl disulphide,* 4·5 g.
In aqueous suspension.					
6	34	—	150	40	Mercaptan,† m. p. 120°.

* M. p. 212° (after crystallisation from glacial acetic acid). Found : Cl = 18·5; S = 17·27. Calc., Cl = 18·8; S = 16·98%.

† Yielding 4 : 4'-dichlorodi-*o*-thioaniline on oxidation with air; m. p. 116°. Found : S = 20·4. Calc., 20·1%.

Reaction of Sodium Trisulphide.

With 1-*Chloro*-2-*nitrobenzene* (I).—*In alcoholic solution* (30 c.c.). 1-Chloro-2-nitrobenzene (6 g.) and sodium trisulphide (6·4 g.), after 3 hours' boiling, gave a yellow precipitate, m. p. 150°, which proved to be a mixture of 2 : 2'-dinitrodiphenyl disulphide and sulphur. The former was purified by repeated crystallisation from glacial acetic acid and extraction with carbon disulphide, the fall in percentage of sulphur with rise in m. p. being as follows : m. p. 168°, S 33%; m. p. 179°, S 30·8%; m. p. 194·5°, S 21·0% (calc. for $VIII_a$, S = 20·77%). By interpolation, a mixture of m. p. 185° would have the sulphur content of 2 : 2'-dinitrodiphenyl trisulphide, whilst, by extrapolation, a mixture of m. p. 160° would correspond with a tetrasulphide. For these reasons, the authors conclude that Blanksma's compounds (*loc. cit.*) are either mixtures or very labile compounds.

In aqueous suspension. The ultimate product was 2 : 2'-diaminodiphenyl disulphide, m. p. 93°. No trithioaniline was obtained.

With 1-*Chloro*-4-*nitrobenzene* (II).—*In alcoholic solution* (30 c.c.). The same results were obtained as in the experiments with suspensions in aqueous sodium disulphide, *viz.*, mixtures of 4 : 4'-dinitrodiphenyl disulphide (both forms) with sulphur were produced and no trithio-compound formed.

In aqueous suspension. From 1-chloro-4-nitrobenzene (2 mols.) and sodium trisulphide (1 mol.) a mixture of 4 : 4'-dinitrodiphenyl mono- and di-sulphides was produced by boiling, but when 15 mols. of the trisulphide were employed (10 g. of II, 152 g. of Na_2S_3, 500 c.c. of water) and the mixture was boiled for 40 hours and then distilled with steam, a residue (4·5 g.), consisting mainly of 4 : 4'-diaminodiphenyl trisulphide, was obtained, and a solution which yielded, after oxidation with air for 2 days, 5 g. of 4 : 4'-*diamino-*

diphenyl trisulphide (XI), m. p. 122° (after crystallisation from alcohol) (Found: S = 34·5. $C_{12}H_{10}N_2S_3$ requires S = 34·29%). The *hydrochloride* melts at about 200° (Found: S = 24·71. $C_{12}H_{10}N_2S_3,2HCl,2H_2O$ requires S = 24·69%). The new trisulphide (XI), which is stable towards carbon disulphide, exhibits a marked tendency to retain sulphur. It is converted by boiling aqueous sodium monosulphide into 4 : 4'-diaminodiphenyl disulphide (X_p), m. p. 78°, and is re-formed from this by means of boiling aqueous sodium trisulphide and subsequent air oxidation. Conversion into X_p is effected also by boiling aniline, with, however, ultimate formation of 4 : 4'-diaminodiphenyl monosulphide. The thiozone group, S_3, is therefore in the para-position to the amino-groups.

With 1 : 4-*Dichloro-2-nitrobenzene* (III).—*In alcoholic solution.* After the reaction (2 mols. of III; 1 mol. of Na_2S_3), the excess of III was removed by steam, and the product, m. p. 185°, repeatedly crystallised from glacial acetic acid and extracted with carbon disulphide; the successive m. p.'s were 190°, 192°, 207°, 212° (Found: in substance, m. p. 212°, Cl = 18·6; S = 17·2. 4 : 4'-Dichloro-2 : 2'-dinitrodiphenyl disulphide, $C_{12}H_6O_4N_2Cl_2S_2$, requires Cl = 18·8; S = 17·0%). Analysis and microscopic examination showed the products melting below 212° to be mixtures of sulphur and the disulphide.

In aqueous suspension. Only 4 : 4'-dichloro-2 : 2'-diaminodiphenyl disulphide could be isolated; no trisulphide was formed.

Analysis of Mixtures of 2-, 3-, *and* 4-*Nitro-1-chlorobenzene.*—The method described by Hodgson and Anderson (J., 1924, **125**, 2195) was first worked out in connexion with this investigation. Sodium trisulphide is the most efficient reagent for the quantitative conversion of 1-chloro-2-nitro- and 1-chloro-4-nitro-benzene into 2- and 4-aminophenyl mercaptans, which are non-volatile with steam, and of 1-chloro-3-nitrobenzene into 3-chloroaniline (volatile with steam).

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LXIV.—*Further Experiments on the Periodic Dissolution of Metals.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

IN addition to the twenty periodic reactions previously described (J., 1924, **125**, 604), involving the liberation of hydrogen, four new reactions are now reported as being periodic under certain conditions. These are (21) magnesium and acetic acid, (22) magnesium and sulphuric acid, (23) magnesium and nitric acid, (24) magnesium and orthophosphoric acid.

Since the most easily reproducible systems are those in which the activating agent is the second metallic component, it seemed desirable to examine these quantitatively. Such systems, however, suffer from the disadvantage that, as a rule, a constant wavelength is not obtained. The *Records 125 and 130* in the previous paper are exceptional in their regularity, and *Records 110 and 111*, which were obtained from couples of magnesium and cobalt and of magnesium and nickel in 10% ammonium chloride solution, give a truer idea of what is usually obtained.

Attempts were therefore made to devise new methods of activation of the metals in order to obtain constant and quantitatively reproducible frequencies. It was taken as a working hypothesis that the irregularity was the result of unequal activation of different parts of the metal surface and that there would be more prospect of obtaining regular waves if a uniform condition of activity over the entire surface were ensured.

Attempts to produce regular waves by polishing the second metallic component with graded emery papers were not successful, but the methods described below were found useful.

Although, as was previously stated, in systems involving the simultaneous use of a colloid, the two metals do not need to be in contact, yet in the purely metallic systems contact between the dissolving metal and the activating metal is necessary. It may be that in the colloid systems the true activating agent is the colloid and not the platinum.

Electro-deposited Metals.—*Record 142* is given in illustration of the regular waves which were obtained by using a surface of electro-deposited copper. Two electrodes of inactive copper were placed in a solution containing 20% of copper sulphate and 5% of sulphuric acid, and a current density of 6·25 amps. per sq. dcm. was used, the deposition being continued for 20 minutes. The activating component consisted of the cathode, placed in contact

with magnesium dissolving in $N/5$-hydrochloric acid.   The copper anode also was active, but its activity soon died out.

Comparative experiments, carried out with current densities varying from 0·625 amp. per sq. dcm. to 6·25 amps. per sq. dcm., indicated that a high current density is desirable, since the resulting waves have a high amplitude.

Chemically Deposited Metals.—Very regular waves can be obtained from the system magnesium and hydrochloric acid by first immersing the magnesium in 0·1% copper sulphate solution for about 5 minutes (*Record 143*) or by dipping it into a dilute stannous chloride solution until a thin deposit forms (*Record 147*).

FIG. 1.
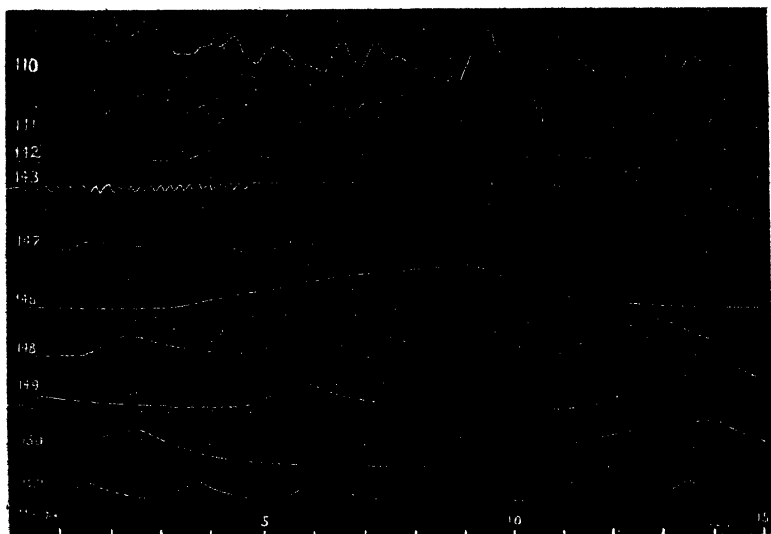
In *Record 143*, the point at which the periodicity ceases coincides with the copper film slipping off the dissolving metal.

· Excellent waves have been obtained by dipping magnesium into solutions of ferrous sulphate or ferrous ammonium sulphate and then dissolving in hydrochloric acid.

Poor results were obtained by depositing nickel from nickel ammonium sulphate solution on magnesium and aluminium, and no improvement was obtained by vacuum-heat treatment.

Regular waves were also obtained by adding to the reacting system about 0·01% of cupric chloride, stannous chloride (*Record 146*), bismuth nitrate (*Record 148*), antimony chloride (*Record 149*), or ferrous sulphate (*Record 150*).

Factors Determining Frequency.—The frequency of the periods is dependent on the concentration of the reagent and on the temperature of the reaction. Keeping these conditions constant, it has been possible, by taking advantage of the regularity of the systems mentioned above, to study the effect of varying the amount of activating material.* Employing the system aluminium and 1·5N-hydrochloric acid, the metal was immersed in 5% copper sulphate solution for time intervals of 90 secs., 30 secs., and 15 secs. before the experiment, and the resulting wave-length was measured. In another series, the effect of the addition to the reacting system of 1 c.c., 0·5 c.c., and 0·2 c.c. of the copper sulphate solution was measured.

The measurements are not given quantitatively, since in the first series the loosely adherent copper film was apt to tear off and in the second series the whole of the reduced metal did not remain in contact with the aluminium, a certain amount being carried into the surrounding liquid by the vigorous evolution of hydrogen.

There is, however, good qualitative evidence from these observations to suggest that low-frequency waves are produced by a large deposit of active copper and that a thin film of the active material gives rise to periods of higher frequency.

Similar results were obtained in the case of copper deposited electrolytically. Copper was deposited, under the conditions already mentioned, for periods of 15, 10, and 5 minutes respectively. When these specimens of activated copper were put in contact with magnesium dissolving in $N/5$-hydrochloric acid, the corresponding durations of a wave were 7, 2·5, and 1 minutes. These results are in accord with the previous statement (*loc. cit.*, p. 623) that in the case of alloys of copper and aluminium dissolving in hydrochloric acid, the alloys rich in copper gave a low frequency.

The Process of Activation.—Further experiments on the activation of metals have strengthened the view, formerly expressed, that the activity is associated with an unstable, close-grained, or possibly amorphous, structure. That there is a real physical difference between two samples of copper sheet before and after activation by scraping is very evident—the metal becomes harder and more brittle. A state of strain at the surface of the metal is indicated by the pronounced concavity of the scraped surface.

Activation of copper has also been effected by cold-rolling. Inactive copper sheet of a thickness of 0·022 in. became active when rolled out to 0·013 in., whilst the sheet obtained by further rolling to a thickness of 0·006 in. produced waves of higher frequency than those derived from the 0·013 in. sheet.

In this connexion reference may be made to what may be termed

" static " periodic properties of metals, which appear to be associated with a state of the metal similar to that which gives rise to the time-periodicity described by the present authors. Thus, Ellis (*J. Inst. Metals*, 1919, **22**, 319) and Johnson (*ibid.*, 1920, **23**, 443) have shown that the progressive cold-rolling of copper is accompanied by periodic changes in certain physical properties. According to Alkins (*ibid.*, 1920, **23**, 438), the susceptibility to corrosion of hard-drawn copper wire varies periodically along the length of the wire and this he ascribes to a periodic difference of electropotential condition along the wire.

In the case of copper deposited electrolytically, it is recognised that the size of the crystal grains becomes smaller with increasing current density (compare Blum, *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 213; 1923, **44**, 397) and it is found that this is just the condition favouring the production of an active surface. Similar conditions appear to apply to chemically deposited metals.

In the method of vacuum-heat treatment, it appears that the change is consequent on the liberation of gas from the surface layers. It has been noticed that with any one piece of metal it is increasingly difficult to bring about activation by this method. With platinum, easy susceptibility to activation can be restored by coating the surface with platinum black. It thus appears that activation depends on the expulsion of gas from the surface molecular layers of the metal. When this has been done, fresh gas is adsorbed only on the outer surface and it becomes increasingly difficult to get gas from the inner layers. Platinising the platinum gives a new start to the process.

Electropotential Measurements.—Experiments at present in progress show that the electropotentials of the inactive and the activated form of the same metal differ considerably. Schmidt (*Z. physikal. Chem.*, 1923, **106**, 105) has shown that the electropotential of most metals is lowered by rubbing with emery paper and he finds a parallelism between the time taken to revert to the normal value and the hardness of the metal. This throws an interesting light on the apparent normal periodic activity of nickel and cobalt (*J.*, 1924, **125**, 622). These metals have been used in the form of rolled sheet and, being among the hardest metals used for this purpose, appear to have still retained the activity imparted by the rolling. This may be contrasted with the behaviour of lead, for although colloidal lead has been of value, massive lead has never yet yielded to any of the methods of activation employed. This appears to be connected with the almost spontaneous annealing of lead at the ordinary temperature.

" Auto-periodic " Systems.—In all the experiments which have

been described hitherto a subsidiary chemical reaction has been used as an indicator of the periodicity inherent in the activated metal (second metallic component). It is, however, possible to make the activated metal itself take part in a chemical reaction. Such "auto-periodic" systems have already been found and attention is being directed to them.

Active Vessels.—" Naturally active " vessels can be produced artificially by leaving glass tubes to soak for long periods in a mixture of colloidal platinum and gelatin in hydrochloric acid. Such tubes have the properties of the original vessel in which the first observations were made, in that no additional activating agent is required. One vessel which had soaked for 3 months gave with aluminium in $3N$-hydrochloric acid *Record 127*. Success in this direction has also been achieved by soaking a vessel in lead acetate solution for 10 months. These observations confirm the view that the natural activity of certain vessels is due to activating material adsorbed on the inner surface.

In many of these cases the production of waves is preceded by an *induction period*, which usually lasts for about $\frac{1}{2}$ hour. The periods do not commence until the initial vigour of the reaction has subsided. This is quite evident in graphs A and C of the previous paper; the records do not illustrate this point, since only small samples cut from the original records are shown. The length of this induction period is very variable and is sometimes as long as 2 hours in colloid systems, whilst it is often absent in systems involving a second metallic component.

Summary.

Four new periodic reactions are given and a study is made of the conditions favouring regular wave formation when metals are used as activating agents. The chief factor appears to be a uniform surface, which is best produced by chemical or electrolytic deposition. In the latter case the effects of varying current density and duration have been studied and the frequency of the waves is found to increase with decreasing amounts of the activating agent. The process of activation has been discussed and further evidence has been adduced to show that the active form of a metal is associated with a close-grained or amorphous structure. Methods for preparing artificially " naturally active " vessels have been given.

LXV.—*The Addition of Ethyl Malonate to Anils.*

By EDWARD JOHNSON WAYNE and JULIUS BEREND COHEN.

BY the action of ethyl acetoacetate on benzylideneaniline, Schiff (*Ber.*, 1898, **31**, 205) obtained an addition compound which he claimed to have isolated in a keto, a keto-enol and an enol form. Similar compounds were obtained from a large number of 1 : 3-diketones, the majority being isolated in three forms (*ibid.*, 605, 1385). Benzylideneaniline was used in these reactions, but Schiff states that all anils may be employed with the exception of salicylideneanils and he gives details of the reaction between benzylidene-β-naphthylamine and ethyl acetoacetate (*ibid.*, 1389). Francis (J., 1899, **75**, 865; 1900, **77**, 1191; 1902, **81**, 441, 956) investigated the addition of dibenzyl ketone and deoxybenzoin to anils, using in addition to benzylideneaniline, benzylidene-*p*-toluidine, *m*-nitrobenzylideneaniline and benzylidene-*m*-nitroaniline. With the substituted anils, much diminished yields were obtained and benzylidene-*o*-toluidine in precisely similar circumstances gave no yield of addition product at all. In view of these observations, it was thought of interest to see if all ortho-substituted anils were incapable of combining with 1 : 3-diketones and to determine in general the effect of substitution. Difficulties in the choice of a suitable diketone, however, soon arose, the majority being unsuitable because of the existence of Schiff's "keto," "keto-enol," and "enol" forms of the product, upon the nature of which subsequent research had thrown doubts. As the result of the work of several investigators, notably Rabe (*Ber.*, 1902, **35**, 3947) and Francis (*Ber.*, 1903, **36**, 937; J., 1904, **85**, 998) it was shown that, although it is probable that two modifications, a "keto" and an "enol" form, exist, it is very difficult, if not impossible, to obtain them in a condition approaching purity, a mixture of the two generally resulting. In some preliminary experiments, in which ethyl acetoacetate, ethyl acetonedicarboxylate, and acetylacetone on the one hand and various anils on the other were used, products of constant melting point could not be obtained. Ethyl malonate was eventually selected as a 1 : 3-diketone, since the products from its union with anils are incapable of existing in tautomeric forms owing to the instability of the grouping $CO_2Et \cdot C:C(OH) \cdot OEt$.

The reaction between ethyl malonate and anils is dependent upon the unsaturated nature of the latter and is formulated :

$$RCH:NX + CH_2(CO_2Et)_2 = R \cdot CH(NHX) \cdot CH(CO_2Et)_2.$$
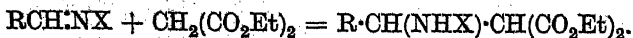
Thus benzylideneaniline and ethyl malonate react to give $Ph \cdot CH(NHPh) \cdot CH(CO_2Et)_2$. The same compound is obtained from aniline and ethyl benzylidenemalonate and was prepared in

this way by Goldstein (*Ber.*, 1895, **28**, 1450), who also made similar compounds from *o*- and *p*-toluidine and phenylhydrazine on the one hand and ethyl benzylidenemalonate on the other. In the following series of experiments the attempt was made to form such addition compounds from a variety of anils and ethyl malonate. The addition compounds so formed have been compared with the same compounds prepared from the appropriate base and ethyl benzylidenemalonate or substituted ethyl benzylidenemalonate wherever possible. A trace of piperidine was generally added to the reaction mixture, as it seemed to hasten the formation of the final product. The results of the experiments seem to show that this reaction is very sensitive to changes in the nature of the radicals attached to the grouping $>$C:N-. In the general formula for anils, R'R''C:NR''', no compound was formed where R''' was aliphatic in nature nor where R'R''R''' were all aromatic. Indeed, compounds with malonic esters could only be obtained from substituted benzylideneanilines and then not in all cases. From phenyl-hydrazones, where R' is NHX, no addition compounds were obtained, although the anticipated product can be made by the addition of phenylhydrazine to ethyl benzylidenemalonate. Benzyl-ideneaniline and benzylidene-*m*- and -*p*-toluidines react most readily. Ortho-substituted benzylideneanilines examined did not react at all with the exception of benzylidene-*o*-aminobenzoic acid. The addition compound could sometimes be prepared from the base and ethyl benzylidenemalonate, and where possible it was made in this way. The nitro-group seems to have an inhibiting effect on the reaction, either no product (*m*-nitrobenzylideneaniline and benzylidene-*p*-nitroaniline) or a small yield (benzylidene-*m*-nitro-aniline) being obtained. This agrees with the observations of Miller and Plöchl (*Ber.*, 1892, **25**, 2056) and of Morgan (J., 1900, **77**, 1210), who found that in the case of the addition of anhydrous hydrogen cyanide to anils the nitro-group either prevented the reaction or diminished the yield. It does not seem to be associated with the character of the nitro-group as a strongly negative radical, since carboxyl-substituted anils react quite readily to give a fair yield of addition product. From ethyl *m*-nitrobenzylidenemalonate and aniline, as also from ethyl benzylidenemalonate and *o*- and *p*-nitroanilines, no product could be isolated, whereas ethyl benzyl-idenemalonate readily reacted with *o*-, *m*-, and *p*-aminobenzoic acids. There is some resemblance between this state of affairs and that which obtains during the formation of the respective anils from the aldehyde and base. Benzaldehyde and *p*-amino-benzoic acid react very readily indeed, with the production of heat and almost immediate formation of the anil, whereas benzylidene-*p*-nitroaniline is one of the most difficult anils to obtain, the reagents

having to be heated for several hours at 140°. The accumulation of substituents seems to diminish the reactivity of anils towards ethyl malonate, for whereas anisylideneaniline gives a good yield of addition compound, both anisylidene-*p*-toluidine and anisylidene-β-naphthylamine fail to give any at all; similarly, *p*-tolylidene-aniline gives an addition compound, whereas *p*-tolylidene-*p*-toluidine does not. In fact, whereas anisylideneaniline and ethyl malonate yield the same compound as is obtained from aniline and ethyl anisylidenemalonate, the latter compound yields with *p*-toluidine and β-naphthylamine the respective anil and ethyl malonate. Anisylideneaniline and benzylidene-*p*-anisidine both gave good yields of addition compound, but none was formed from the corresponding *o*-methoxy-compounds. By prolonged heating at 100°, salicylideneaniline and ethyl malonate gave a small quantity of a compound with a m. p. considerably higher than those usually obtained for these addition compounds. On examination, it proved to be the anilide of coumarincarboxylic acid and was identified by comparison with specimens prepared from both coumarincarboxylic acid and ethyl coumarincarboxylate and aniline.

$$C_6H_4{<}^{OH}_{CH:NPh} + CH_2(CO_2Et)_2 \rightarrow C_6H_4{<}^{O-CO}_{CH:C(CO_2Et)} +$$
$$EtOH + PhNH_2 \rightarrow C_6H_4{<}^{O-CO}_{CH:C(CO\cdot NHPh)} + EtOH.$$
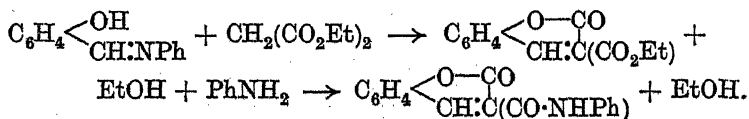
A similar result was obtained with salicylidene-*p*-toluidine, which gave the *p*-toluidide of coumarincarboxylic acid. The first stage of the reaction as formulated above, *i.e.*, the production of a substituted benzylidene ester *plus* the amine from the anil and ethyl malonate, was also observed in the case of *p*-dimethylaminobenzylidene-aniline and -β-naphthylamine, where by the action of ethyl malonate on the anil in the presence of piperidine a little ethyl *p*-dimethylaminobenzylidenemalonate was isolated along with much unchanged anil. It was found impossible to obtain any addition compound in the case of anils substituted with the basic dimethyl-amino-group. Indeed ethyl benzylidenemalonate and dimethyl-*p*-phenylenediamine (*p*-aminodimethylaniline) react very readily in the cold to give the anil and ethyl malonate. Ethyl *p*-dimethyl-aminobenzylidenemalonate and aniline, on heating for 3—4 hours at 100°, yielded the anil. It thus appears that this reaction is to some extent reversible, as in the presence of piperidine the production of the substituted benzylidene ester from the anil and ethyl malonate was observed. Knoevenagel (*Ber.*, 1898, **31**, 2596), by heating anils and malonic acid, found that in general the amine together with the corresponding benzylidenemalonic acid (or cinnamic acid by loss of carbon dioxide) was produced.

In view of the fact that Francis and Taylor (*Ber.*, 1903, **36**, 941) observed that methyl acetoacetate and benzylideneaniline reacted much less readily than the ethyl ester with the production of a very much smaller amount of addition product (only about 16% of pure product), the reaction between methyl malonate and benzylideneaniline was investigated. In this case, the addition compound was obtained with equal ease and with only slightly less yield than in the case of the ethyl ester. Similar results were obtained with benzylidene-*m*- and -*p*-toluidines; with benzylidene-*o*-toluidine and methyl malonate, as with the ethyl ester, no reaction took place. Menthyl malonate, which was also used in a reaction of this type, gave a much smaller yield of addition product with benzylideneaniline. Francis (J., 1904, **85**, 998) succeeded in obtaining an addition compound from ethyl methylacetoacetate and benzylideneaniline. From ethyl ethylmalonate, as also from ethyl nitromalonate, and benzylideneaniline it was found impossible, in spite of several attempts, to obtain any addition compound.

The following is a list of anils which have been investigated in their reaction with malonic esters together with the m. p. and approximate yield, usually the average of two experiments, of the product.

Ethyl Malonate.

Anil.	Yield %.	M. p.
Benzophenone anil	None	—
Benzylidenemethylamine	,,	
„ -aniline	85	100—101°
,, -*o*-toluidine	None	67—68 *
,, -*m*-toluidine	80	91—92
,, -*p*-toluidine	,,	80—82
,, -2 : 4-xylidine	None	—
,, -α-naphthylamine	,,	91·5—92 *
,, -β-naphthylamine	40	129—130
p-Tolylidene-aniline	50	88—90
„ -*p*-toluidine	None	—
Benzylidene-*o*-nitroaniline	,,	—
,, -*m*-nitroaniline	15	99—101
,, -*p*-nitroaniline	None	—
m-Nitrobenzylideneaniline	,,	—
Benzylidene-*o*-aminobenzoic acid	45	116—117·5
,, -*m*-aminobenzoic acid	40	137—137·5
,, -*p*-aminobenzoic acid	,,	164—164·5
,, -*p*-bromoaniline	45	84·5—85·5
,, -*p*-chloroaniline	40	81—82
Salicylideneaniline	Gave coumarincarboxyanilide.	
„ -*p*-toluidine	Gave coumarincarboxy-*p*-toluidide.	
o-Methoxybenzylideneaniline	None	—
p-Methoxybenzylideneaniline	60	81—82·5
Benzylidene-*o*-methoxyaniline	None	68—68·5 *
„ -*p*-methoxyaniline	65	97—99
p-Methoxybenzylidene-*p*-toluidine	None	—
„ -β-naphthylamine	,,	—
p-Dimethylaminobenzylideneaniline	,,	—
„ -β-naphthyl-amine	,,	—
Benzylidene-*p*-aminodimethylaniline		—

Menthyl malonate.

Anil.	Yield %.	M. p.
Benzylideneaniline	10—15	200—201

Methyl malonate.

Benzylidene-aniline	65	114·5
„ -*o*-toluidine	None	—
„ -*m*-toluidine	70	107—108·5
„ -*p*-toluidine	70	120—121

* These are the m. p.'s of the anticipated compound made by the addition of the amine to the ethyl benzylidenemalonate.

EXPERIMENTAL.

The general method employed was to add a slight excess of ethyl or methyl malonate plus a small amount (0·05 to 0·2 c.c.) of piperidine to the anil, warming until solution or melting took place. The liquid so obtained in a few cases yielded the addition compound on standing, but in general it had to be heated on the water-bath for periods varying from 1 to 20 hours. The addition compound separated out on cooling and allowing to stand in some cases ; in others, the unchanged anil (if a solid) separated out. In the case of liquid anils which had not reacted, a considerable amount could usually be recovered as the picrate, it being observed that anils (excepting carboxy-substituted anils) form picrates very readily whereas the malonic ester addition compounds fail to do so at all. In cases where the m. p. of an anil and of its malonic ester addition product did not differ considerably, this property afforded a useful test. In preparing the addition compounds for comparison from ethyl benzylidenemalonate and the appropriate base, the two, dissolved in a little solvent (usually benzene or methyl alcohol), were left at the ordinary temperature for some time. If no reaction product separated, the solvent was evaporated and the mixture heated on the water-bath for some hours. The identity of the product obtained by the two different methods was ensured by the similarity of crystalline form and by mixed m. p. determinations.

Ethyl β-Anilinobenzylmalonate.—Equal weights of benzylidene-aniline and ethyl malonate were left at the ordinary temperature for 24 hours, when the mass became solid. Recrystallised from alcohol, the compound was obtained in 85% yield. It agreed in its properties with that obtained from ethyl benzylidenemalonate and aniline by Goldstein (*Ber.*, 1895, **28**, 1450) (Found : N = 4·21. Calc., N = 4·12%). It is not, however, so soluble in alcohol as he seems to indicate. It may be obtained in 50% yield by heating equivalent amounts of benzaldehyde, aniline, and ethyl malonate on the water-bath with a little piperidine for 2—3 hours. On

rendering an aqueous solution of the potassium salt just acid with dilute acetic acid, a precipitate having the m. p. and properties of benzylideneaniline was gradually produced. Goldstein (*loc. cit.*) states that benzaldehyde, aniline, and malonic acid are obtained in this way. On distillation in a vacuum (30 mm.), the ester decomposes completely into benzylideneaniline and ethyl malonate.

Ethyl β-o-*toluidinobenzylmalonate* was obtained in the same way as by Goldstein (*loc. cit.*); m. p. 67—68°. Benzylidene-*o*-toluidine and ethyl malonate yielded no addition compound even on seeding, and after 5 hours' heating on the water-bath 90% of anil was recovered as the pale yellow picrate, m. p. (with blackening) 203—205°.

Ethyl β-m-*Toluidinobenzylmalonate.*—Benzylidene-*m*-toluidine (1·2 g.) and ethyl malonate (1·0 g.) were left at room temperature for 24 hours, when the mass solidified. Recrystallised from alcohol, 80% of addition compound was obtained as colourless needles, m. p. 91—92°. Ethyl benzylidenemalonate and *m*-toluidine in molecular proportions yielded the same product on standing for 24 hours (Found : N = 4·08. $C_{21}H_{25}O_4N$ requires N = 3·94%). The hydrochloride formed by passing dry hydrogen chloride into an ethereal solution separates as colourless needles, m. p. 103—105°.

From neither benzylidene-2 : 4-xylidine and ethyl malonate nor from ethyl benzylidenemalonate and 2 : 4-xylidine could addition compounds be obtained.

Ethyl β-α-*naphthylaminobenzylmalonate* could not be obtained from the anil. α-Naphthylamine (0·8 g.) and ethyl benzylidene-malonate (1·4 g.) were heated on the water-bath for 6—8 hours and left to stand several days, when the addition compound gradually separated. After two recrystallisations from alcohol, it was obtained as colourless, odourless, irregular prisms, m. p. 91·5—92° (Found : N = 3·76. $C_{24}H_{25}O_4N$ requires N = 3·58%).

Ethyl β-β-*Naphthylaminobenzylmalonate.*—Benzylidene-β-naphthylamine (0·8 g.) and ethyl malonate (0·5 g.) were heated on the water-bath for 20 hours. On cooling, the addition product separated mixed with unchanged anil. It forms colourless, matted needles (from alcohol), sparingly soluble in cold, readily in hot, alcohol; m. p. 129—130° (Found : N = 3·59. $C_{24}H_{25}O_4N$ requires N = 3·58%). The same compound was obtained by heating molecular proportions of ethyl benzylidenemalonate and β-naphthylamine on the water-bath for an hour, or benzaldehyde, β-naphthylamine, ethyl malonate and a little piperidine for 8 hours.

Ethyl β-*Anilino*-p-*tolylmalonate.*—p-Tolylideneaniline (1·0 g.) and ethyl malonate (0·8 g.), heated at 100° for 6 hours, yielded the addition compound on allowing to stand and scratching vigorously.

It forms colourless needles from alcohol, m. p. 88—90°. Yield 50% (Found : N = 3·95. $C_{21}H_{25}O_4N$ requires N = 3·94%).

Benzylidene-o-nitroaniline and ethyl malonate, heated at 100° for 2—3 hours, yielded the unchanged anil. Longer heating yielded some o-nitroaniline. From o-nitroaniline and ethyl benzylidene-malonate no compound could be obtained.

Ethyl β-m-*Nitroanilinobenzylmalonate.*—Benzylidene-m-nitroanil-ine (0·9 g.) and ethyl malonate (0·6 g.) were heated for 12 hours on the water-bath. On standing, a mixture of addition compound and unchanged anil separated. Three recrystallisations from alcohol yielded sulphur-yellow, matted needles, m. p. 105—106°. Yield 15% (Found : N = 7·35. $C_{20}H_{22}O_6N_2$ requires N = 7·25%). Ethyl benzylidenemalonate (1·3 g.) and m-nitroaniline (0·8 g.) yielded the same product in 40% yield by mixing hot alcoholic solutions and allowing to stand for a day.

From neither m-nitrobenzylideneaniline and ethyl malonate nor from ethyl m-nitrobenzylidenemalonate and aniline could an addition compound be obtained in spite of several attempts. Considerable tendency to form a sticky product was shown in both cases.

Ethyl β-o-*Carboxyanilinobenzylmalonate.*—Benzylideneanthranilic acid (0·8 g.) and ethyl malonate (0·55 g.), heated for 8 hours at 100°, yielded this compound on standing. Purified by precipitating a benzene solution with ligroin, it forms small prisms. It may be crystallised from alcohol, in which it is very soluble. Yield 45%, m. p. 116—117·5° (Found : N = 3·93. $C_{21}H_{23}O_6N$ requires N = 3·73%). Ethyl benzylidenemalonate (1·3 g.) and anthranilic acid (0·7 g.), heated for 5 hours at 100°, yield the same product.

Ethyl β-m-*Carboxyanilinobenzylmalonate.*—Benzylidene-m-amino-benzoic acid (0·8 g.) and ethyl malonate (0·6 g.), heated for 5 hours at 100°, yielded the addition compound on seeding in 40% yield. Recrystallised twice from alcohol, it forms needles, m. p. 137—137·5° (Found : N = 3·68. $C_{21}H_{23}O_6N$ requires N = 3·73%). From ethyl benzylidenemalonate (1·3 g.) and m-aminobenzoic acid (0·7 g.) dissolved in hot alcohol and left to stand for a day, the compound was obtained in 80% yield.

Ethyl β-p-*Carboxyanilinobenzylmalonate.*—Benzylidene-p-amino-benzoic acid (1·2 g.) and ethyl malonate (1·2 g.), heated at just below the b. p. of the ethyl malonate till solution had occurred and then at 150° for ½ hour and finally on the water-bath for 8 hours, yielded a viscous mass, from which the addition compound was obtained on scratching and seeding. Recrystallised twice from alcohol, colourless, short needles, m. p. 164—164·5°, were obtained. Yield 40% (Found : C = 64·37; H = 6·1. $C_{21}H_{23}O_6N$ requires

C = 64·54; H = 6·13%).   Hot alcoholic solutions of ethyl benzyl-
idenemalonate (1·3 g.) and p-aminobenzoic acid (0·7 g.) yielded
70% of this compound on standing for a day.   On treatment of
an ethereal solution with dry hydrogen chloride, no hydrochloride
could be obtained from this compound, probably on account of its
acid character.

Ethyl β-p-*Chloroanilinobenzylmalonate.*—Benzylidene-p-chloroanil-
ine (1·1 g.) and ethyl malonate (0·8 g.), heated for 8 hours at 100°,
yielded 40% of addition compound.   Recrystallised from methyl
alcohol, it forms colourless needles, m. p. 81—82° (Found : N = 3·77.
$C_{20}H_{22}O_4NCl$ requires N = 3·73%). p-Chloroaniline, heated with
twice its weight of ethyl benzylidenemalonate at 100° for 3 hours,
gave the same compound.

Ethyl β-p-*Bromoanilinobenzylmalonate.*—Benzylidene-p-bromoanil-
ine (1·2 g.) and ethyl malonate (0·8 g.), heated at 100° for 6 hours,
yielded 45% of addition compound.   Recrystallised twice from
alcohol, it forms colourless needles, m. p. 84·5—85·5° (Found :
N = 3·41. $C_{20}H_{22}O_4NBr$ requires N = 3·33%).   The same com-
pound is obtained from ethyl benzylidenemalonate (1·2 g.) and
p-bromoaniline (1·1 g.), heated for 3 hours at 100°.

Action of Ethyl Malonate on Salicylidencaniline and Salicylidene-
p-*toluidine.*—Salicylideneaniline and ethyl malonate in molecular
amounts were warmed on the water-bath with a little piperidine
for 24 hours.   A small amount of a substance very sparingly soluble
in boiling alcohol gradually separated, m. p. 238—240°.   The same
substance was produced by heating molecular proportions of ethyl
coumarincarboxylate and aniline on the water-bath for 24 hours,
when the product was gradually deposited from the hot mixture.
It was separated from unchanged ester by extraction of the latter
with boiling alcohol and recrystallised from much ethyl acetate.
It forms yellow needles, m. p. 240—241·5°, and is only very slightly
soluble in ordinary solvents.   Coumarincarboxylic acid and aniline
react in a precisely similar fashion.   The product is the anilide of
coumarincarboxylic acid (Found : N = 5·25.   Calc. for $C_{16}H_{11}O_3N$,
N = 5·28%).   The substance is mentioned (D.R.-P. 172,724, 1905)
as the product of the action of benzaldehyde on malonanilide, m. p.
250° (no analysis given).

In precisely similar fashion, salicylidene-p-toluidine yields the
p-toluidide of coumarincarboxylic acid.   Ethyl coumarincarboxylate
and p-toluidine, heated at 100° for 24 hours, yield the same product
in larger quantity.

The p-*toluidide of coumarincarboxylic acid* is insoluble in the cold
in alcohol, ether, benzene, or ligroin.   It is slightly soluble in hot
alcohol and more soluble in boiling ethyl acetate, from which it

can be crystallised. It forms yellow needles, m. p. 220—222° (Found : N = 5·02. $C_{17}H_{13}O_3N$ requires N = 5·10%).

Ethyl β-Anilinoanisylmalonate.—Anisylideneaniline (1 g.) and ethyl malonate (0·8 g.) were heated for 12 hours at 100°. The compound deposited after keeping for a week was dissolved in a little benzene, in which it is very soluble, and ligroin added in considerable excess. After two such treatments, it was obtained as colourless needles, m. p. 81—82·5°. Yield 60% (Found : N = 3·88. $C_{21}H_{25}O_5N$ requires N = 3·77%). The same compound was prepared by heating anisylidenemalonic ester (1·4 g.) and aniline (0·7 g.) at 100° for 2—3 hours. Yield 20%.

Ethyl β-o-anisidinobenzylmalonate could not be obtained from the anil and ethyl malonate, but was prepared by heating o-anisidine (1·25 g.) with ethyl benzylidenemalonate (2·5 g.) for 6 hours at 100°. The product separated out after several weeks and was crystallised from a mixture of two parts of benzene and one of ligroin. Colourless prisms, m. p. 68—68·5°, were thus obtained, very soluble in alcohol, ether, or benzene, less soluble in ligroin (Found : N = 3·82. $C_{21}H_{25}O_5N$ requires N = 3·77%).

Ethyl β-p-anisidinobenzylmalonate was obtained from benzylidene-*p*-anisidine (0·75 g.) and ethyl malonate (0·6 g.) after 4 hours' heating at 100°. Recrystallised from methyl alcohol, it forms colourless needles, m. p. 97—99°. Yield 65% (Found : N = 3·93. $C_{21}H_{25}O_5N$ requires N = 3·77%). From molecular quantities of ethyl benzylidenemalonate and *p*-anisidine in hot methyl alcohol the same product separates, after 24 hours' standing, in 55% yield.

Action of Ethyl Anisylidenemalonate on p-*Toluidine and* β-*Naphthylamine.*—Anisylidene-*p*-toluidine and anisylidene-β-naphthylamine yielded unchanged anil after several hours' heating with ethyl malonate. Ethyl anisylidenemalonate (0·7 g.) and *p*-toluidine (0·35 g.), heated for 5 hours on the water-bath, yielded, on cooling, a solid, proved to be identical with anisylidene-*p*-toluidine by mixed m. p. determinations on the compounds and the picrates. Anisylidene-*p*-toluidine picrate is yellow and separates from alcohol in needles, m. p. 178—180°. Ethyl anisylidenemalonate and β-naphthylamine react similarly. The picrate of the anil is yellow; m. p. 185—186°.

Action of Ethyl p-*Dimethylaminobenzylidenemalonate on Aniline and* β-*Naphthylamine.*—On heating *p*-dimethylaminobenzylidene-aniline (1·1 g.) and ethyl malonate (0·8 g.) for 8—10 hours at 100° in the presence of piperidine, no addition compound could be detected, but a small amount (about 0·1 g.) of ethyl *p*-dimethyl-aminobenzylidenemalonate was obtained. On heating the latter compound with aniline on the water-bath with or without piperidine,

the anil was obtained and identified by a mixed m. p. determination and the formation of the picrate. With β-naphthylamine and its anil, similar results were obtained.

Ethyl p-*Dimethylaminobenzylidenemalonate.*—p-Dimethylamino-benzaldehyde (3 g.) and ethyl malonate (3·2 g.) with the addition of 5 drops of piperidine were heated on the water-bath for 16 hours. Recrystallised twice from alcohol, glistening, light yellow prisms were obtained, m. p. 110—110·5°. Yield 55% (Found : N = 4·96. $C_{16}H_{21}O_4N$ requires N = 4·81%).

Benzylidenemalonic ester (0·40 g.) and p-aminodimethylaniline (0·65 g.), on mixing in the cold, immediately deposited the anil, which was identified by the usual tests.

Menthyl β-*Anilinobenzylmalonate.*—Benzylideneaniline (1 g.) was heated with menthyl malonate (2 g.) (Hilditch, J., 1909, **95**, 1579) and a trace of piperidine for 6 hours at 100°, when the addition compound separated from the hot mixture. The unchanged anil and ester were dissolved out with hot alcohol, in which the product is practically insoluble. Purified by dissolving in warm benzene and precipitating with ligroin, it was obtained in matted needles, m. p. 200—201°. The yield was only 10% in one experiment and 15% in another. The same product was obtained by warming menthyl benzylidenemalonate and aniline on the water-bath for ½ hour (Found : C = 76·4; H = 8·86. $C_{36}H_{51}O_4N$ requires C = 77·0; H = 9·1%).

Menthyl benzylidenemalonate was prepared by heating 2 g. of menthyl malonate and 0·5 g. of benzaldehyde with the addition of 0·2 c.c. of piperidine for 6 hours at 100°. The product separated from alcohol in short needles, m. p. 94·5—95·5°. Yield 40% (Found : C = 77·12; H = 9·6. $C_{30}H_{44}O_4$ requires C = 76·93; H = 9·4%).

Methyl β-*Anilinobenzylmalonate.*—Benzylideneaniline (0·9 g.) and methyl malonate (0·7 g.) were kept for 24 hours at the ordinary temperature, when a solid mass was obtained. Recrystallised twice from methyl alcohol, small needles, m. p. 114—115°, in 65% yield, were obtained agreeing in properties with the compound obtained by Blank (*Ber.*, 1895, **28**, 146) by the addition of aniline to methyl benzylidenemalonate.

Methyl β-m-*Toluidinobenzylmalonate.*—Benzylidene-*m*-toluidine (1 g.) and methyl malonate (0·7 g.) yielded the compound in 70% yield after 2 days' standing. Purified twice by addition of ligroin to a cold benzene solution, colourless needles, m. p. 107—108·5°, were obtained (Found : N = 4·39. $C_{19}H_{21}O_4N$ requires N = 4·28%).

Methyl β-p-*toluidinobenzylmalonate*, prepared in precisely similar fashion in 70% yield, separated as colourless needles, m. p. 120—121° (Found : N = 4·41. $C_{19}H_{21}O_4N$ requires N = 4·28%).

The following anils are not described in the literature. p-*Dimethylaminobenzylidene* - β - *naphthylamine.*—p -Dimethylaminobenzaldehyde (1·5 g.) and β-naphthylamine (1·4 g.), dissolved in hot alcohol, were mixed, when the product separated immediately. Recrystallised from much alcohol, bright yellow needles were obtained, m. p. 164—165° (Found : N = 10·02. $C_{19}H_{18}N_2$ requires N = 10·21%).

p-*Dimethylaminobenzylidene*-p-*aminobenzoic acid,* prepared by mixing hot alcoholic solutions of the components, using 0·9 g. of aminoacid to 1·1 g. of aldehyde, separated immediately as irregular crystals, m. p. 261—262° (decomp.). It is insoluble in hot or cold benzene, chloroform, or ligroin and sparingly soluble in hot alcohol (Found : N = 10·6. $C_{16}H_{16}O_2N_2$ requires N = 10·45%).

Anisylidene-p-*aminobenzoic acid* was obtained by mixing hot alcoholic solutions of anisaldehyde (1·9 g.) and p-aminobenzoic acid (2·0 g.). From alcohol, it separates in tufts of needles, m. p. 194—195° (Found : N = 5·58. $C_{15}H_{13}O_3N$ requires N = 5·49%).

Benzylidene-m-*toluidine* is described by Law (J., 1912, **101**, 158) as a liquid boiling at 315°. By using purified benzaldehyde and m-toluidine, a solid was obtained, m. p. 30—32°, very soluble in all organic solvents.

p-*Tolylideneaniline,* also prepared by Law (*loc. cit.*), was obtained as a solid, m. p. 46·5—48°, after freeing from liquid by pressing on porous plates. It also is extremely soluble in all ordinary organic solvents.

LXVI.—*The Chemistry of the Glutaconic Acids. Part XVIII. Three-carbon Tautomerism in the cyclo-Propane Series. Part IV.*

By FRANK ROBERT GOSS, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

ALTHOUGH the isomerism of the glutaconic acids has been under investigation for some time, interest has centred recently around cyclic glutaconic acids, such as the acid represented by formula (I) or (II), since it has been shown that the characteristics of glutaconic isomerism reappear even although geometrical isomerism is

excluded by ring formation (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342; 1924, **125**, 1927).

$$CH_3 \cdot C \overset{\displaystyle C \cdot CO_2H}{\underset{\displaystyle C \cdot CO_2H}{\big|_H}} \qquad CH_3 \cdot C \overset{\displaystyle CH \cdot CO_2H}{\underset{\displaystyle C \cdot CO_2H}{<}} \qquad CH_3 \cdot CH \overset{\displaystyle C \cdot CO_2H}{\underset{\displaystyle C \cdot CO_2H}{<}}$$

(I.)   (II.)   (IIa).
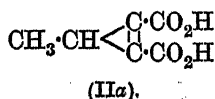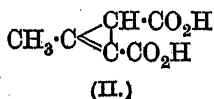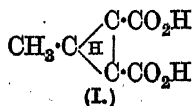
The acid occurs in one form, m. p. 200°, and although its addition reactions are fully explicable by means of formula (II), the non-committal formula (I) is used to recall the fact that this acid, in common with other glutaconic acids containing a mobile α-hydrogen atom, gives rise to certain derivatives which conventional symbols cannot explain. Thus there are three series of esters. The so-called "normal" esters are most closely related to the acid and hence are given the special formula (III), although their addition reactions (which in certain cases have been proved to occur without previous isomeric change) are explicable by means of formula (IV). This formula is reserved to distinguish the so-called "labile" esters, the addition products of which (so far as has yet been found) are identical with those of the corresponding normal esters. The "enol" esters have formula (V); they are yellow and weakly acidic, giving rise to yellow sodium salts and red iron salts. On the other hand, the "normal" and "labile" esters are colourless, neutral substances. The three series of esters are reversibly inter-convertible, the labile esters forming the connecting link between the other two series.

(III.) $CH_3 \cdot C \overset{\displaystyle C \cdot CO_2R}{\underset{\displaystyle C \cdot CO_2R}{\big|_H}}$ $CH_3 \cdot C \overset{\displaystyle CH \cdot CO_2R}{\underset{\displaystyle C \cdot CO_2R}{<}}$ (IV.)

(V.) $CH_3 \cdot C \overset{\displaystyle C:C(OH) \cdot OR}{\underset{\displaystyle C \cdot CO_2R}{<}}$ $CH_3 \cdot CH \overset{\displaystyle C \cdot CO_2R}{\underset{\displaystyle C \cdot CO_2R}{<}_H}$ (IVa.)
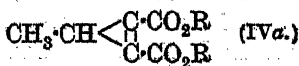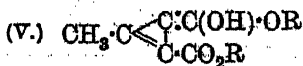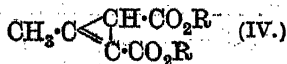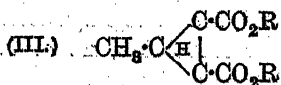
It is necessary to direct attention once again to these facts, because, in a recent communication (*Annalen*, 1924, **436**, 135), Feist, whilst admitting that he has not yet prepared enough of the parent acid to be able to repeat any of this work on its esters, nevertheless expresses a general incredulity, not only as to our interpretation of the data, but also as to the facts themselves.* We have therefore repeated all the more important experiments described in our earlier papers, and have now to reaffirm that, so far as we are yet aware, the experimental facts previously recorded by us are accurate; that, in particular, there is but one acid,

* "Die Existenz einer Enolform ist an sich unwahrscheinlich," etc. (*loc. cit.*).

although this gives rise to three series of esters related to the acid and to one another in the manner indicated.

Identity of the Acid.

Feist's previous view that there are two isomeric acids, m. p.'s 200° and 189°, having formulæ (II) and (IIa), has now undergone modification, since he has found that the preparation having m. p. 189° displays reactions identical with those of the acid, m. p. 200°. There are therefore, according to Feist, two acids of formula (II), the modification having m. p. 189° being produced by the reduction of the bromine-addition product of the form of m. p. 200°. We cannot confirm this result. We have repeated the experiment many times and have failed to detect any indication of the formation of a second isomeride. It is true that the crude reduction product, prepared under the conditions described by Feist, often melts about 10—12° too low, but this is easily understood, since it contains, as a somewhat persistent impurity, a more fusible, saturated acid differing in empirical composition by two hydrogen atoms only. It is not easy to accomplish complete purification by crystallisation from water, but careful crystallisation from ether and certain other solvents quickly raises the m. p. to 200°. Feist's supposed acid of m. p. 189° is therefore merely an impure preparation of the acid of m. p. 200°.* Naturally, all mixtures of the pure and impure speciments melt between the m. p.'s of their constituents; both pure and impure forms yield the same crystalline dibromide, m. p. 244°, the same methyl ester,† m. p. 32°, the same ethyl ester,† m. p. 38—39°, and the same methyl ester dibromide, m. p. 77°. Feist claims to have observed small differences of m. p. amongst these derivatives, and also minute mixed-melting-point depressions. These small differences and depressions we have searched for and have been completely unable to observe.‡

* Compare Goss, Ingold, and Thorpe, J., 1923, 123, 339—340.
† Prepared through the silver salts as Feist describes.
‡ The following data may assist independent judgment as to the existence of these isomerides :

| Derivative. | Recorded by Feist (l. c.). | | | Our observations. |
	From acid, m. p. 200°.	From "acid, m. p. 189°."	Mixture.	Both preparations and mixture.
	M. p.	M. p.	M. p.	M. p.
Dibromide	244°	232°	234°	244°
normal Methyl ester	32	30·5	29—30	32
normal Ethyl ester	38	38	37—37·5	38—39
Methyl ester dibromide	77	72	(not recorded)	77

The Isomeric Esters.

Feist has called in question the existence of the " enol " esters (V), but his remarks on this point (p. 461, footnote) may perhaps be disregarded, since he has not yet attempted to repeat their preparation.

Feist further suggests that the " labile " isomerides have a different constitution, viz., the symmetrical formula (IVa), the " normal " esters having formula (IV). New evidence on this point is submitted in this paper, but it may be pointed out that we have already placed on record observations (disregarded by Feist) which prove that the labile esters cannot have the symmetrical constitution, since their addition products, which are identical with the addition products of the " normal " esters, are always of type (VI), never of type (VIa). It cannot be argued that the labile esters pass into normal esters prior to addition, because in some cases addition occurs to the labile esters more readily than to their normal isomerides. Further, the labile esters, despite their name, are really very stable,—a great deal more so than this type of hypothesis would require. Further, the addition product is still of type (VI), even although the addendum is one which should more readily attack the symmetrical structure (IVa) than the unsymmetrical structure (IV) (vide infra).

$$\text{(VI.)} \quad CH_3 \cdot CX \begin{cases} CY \cdot CO_2H \\ CH \cdot CO_2H \end{cases} \qquad CH_3 \cdot CH \begin{cases} CX \cdot CO_2H \\ CY \cdot CO_2H \end{cases} \text{(VIa.)}$$

$$\text{(Addendum} = X - Y)$$
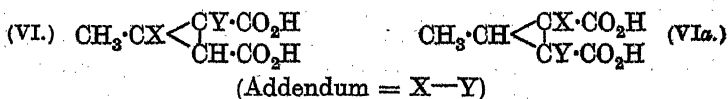
Final proof, if that were needed, that the " labile " esters cannot have the symmetrical formula is furnished by the observation that they can exist in optically active forms. Further, the fact that the " normal " esters, and, as Feist himself showed, the parent acid, can also display optical activity strikingly confirms the chemical evidence that the symmetrical structure (IIa and IVa) does not in any way enter into the chemistry of these substances.

These considerations must also form an important check on all future speculations regarding the structure of the " normal " and " labile " glutaconic esters; for they prove that the mobile hydrogen atom does not occupy, and, under ordinary conditions, cannot even pass through, a completely symmetrical position.

Mobility of the Three-carbon System.

One of the most remarkable characteristics of glutaconic iso-merism is that it can co-exist with tautomeric mobility, which, it must be supposed, would destroy any definite geometrical arrange-ment around the double linking. This indeed is one of the many

difficulties in the way of a geometrical interpretation of the iso-merism. The facts of the case are clearly brought out in the unsymmetrically substituted glutaconic esters such as αβ-dimethyl-glutaconic ester, to which, for the reason stated below amongst others, both formula (VII) and (VIII) must be given. This ester, moreover, exists in two well-defined forms, which are stable iso-merides and show little or no tendency to undergo interconversion even at moderately high temperatures. *Both* these forms react as though *each* had *both* formulæ; thus on treatment with ozone in a neutral solvent in the cold (Feist and Bauer, *Annalen*, 1922, 428, 68), each yields a mixture of the same two ozonides, (IX) and (X) :

$$CO_2Et \cdot CHMe \cdot CMe:CH \cdot CO_2Et \rightleftharpoons CO_2Et \cdot CMe:CMe \cdot CH_2 \cdot CO_2Et$$

(VII.) | (two forms) | (VIII.)

(IX.) $CO_2Et \cdot CHMe \cdot CMe \cdot CH \cdot CO_2Et$ $CO_2Et \cdot CMe \cdot CMe \cdot CH_2 \cdot CO_2Et$ (X.)

           $\diagdown O_3 \diagup$ $\diagdown O_3 \diagup$
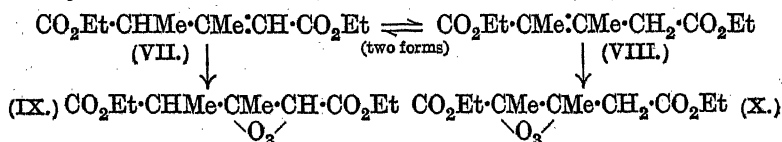
It is not possible, of course, to supply the same kind of proof of mobility in the case of symmetrically substituted glutaconic esters such as the esters (" normal " and " labile ") of the acid (I); but, in view of the fact that the main characteristics of the iso-merism are reproduced throughout the series, the evidence obtained in the unsymmetrical cases must be regarded as bearing also on the symmetrical ones, including the cyclic individuals under discussion.

Some new experiments confirming this conclusion are now recorded. The object of these was to synthesise isomeric acid-esters of the types (XI) and (XII) by the methods employed to obtain similar isomeric derivatives of camphoric acid and other dibasic acids in which the two carboxyl groups are not equivalent. The products, however, proved to be not isomeric but identical.

(XI.) $CH_3 \cdot C \diagdown^{CH \cdot CO_2R}_{C \cdot CO_2H}$ $CH_3 \cdot C \diagdown^{CH \cdot CO_2H}_{C \cdot CO_2R}$ (XII.)
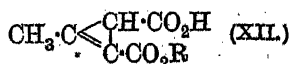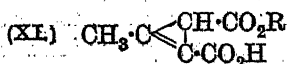
Constitution of the Methyl Alcohol Addition Product.

A strict proof of the constitution of this substance is of import-ance, because methyl alcohol is an addendum which would be expected to combine more readily * with the symmetrical individual

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  * Note the greater additive power of esters of the type of fumaric ester, $CO_2R \cdot CH:CH \cdot CO_2R$, as compared with those of the type of crotonic ester, $CH_3 \cdot CH:CH \cdot CO_2R$, towards addenda (H)–X. Perkin and Thorpe (J., 1901, 79, 729) found that the reaction

     $CH_3 \diagdown_{\diagdown} C:C \diagup^{C \cdot CO_2Et}_{C \cdot CO_2Et}$ + EtOH $\longrightarrow$ $CH_3 \diagdown_{\diagdown} C \diagup^{C(OEt) \cdot CO_2Et}_{CH \cdot CO_2Et}$
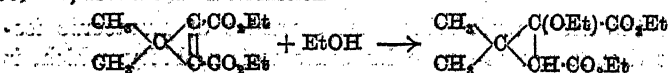
took place with such ease that perceptible combination occurred even in dilute aqueous solution.

(IVa) than with the unsymmetrical compound (IV); so that if (IVa) existed in solution, even as a phase in a tautomeric mixture, its presence would be shown by the formation of the addition product (XIII) rather than of (XIV).

$$(\text{XIII.}) \quad CH_3 \cdot CH \begin{smallmatrix} C(OMe) \cdot CO_2H \\ CH \cdot CO_2H \end{smallmatrix} \qquad CH_3 \cdot C(OMe) \begin{smallmatrix} CH \cdot CO_2H \\ CH \cdot CO_2H \end{smallmatrix} (\text{XIV.})$$
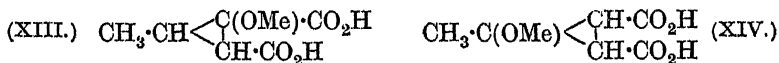
The reaction used for the orientation of the methoxyl group was the now well-known isomeric change of hydroxy*cyclo*propanes into open-chain ketones :

$$ C \begin{smallmatrix} C \cdot O(H) \\ C \end{smallmatrix} \longrightarrow C \begin{smallmatrix} C:O \\ C(H) \end{smallmatrix} $$
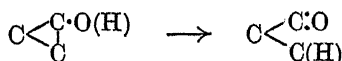
Fuming hydrochloric acid was employed, so that the methoxyl group was first hydrolysed to hydroxyl. The ketones to be expected from the two methoxy-acids (XIII) and (XIV) are α-keto-β-methyl-glutaric acid (XV) and acetosuccinic acid (XVI) respectively, but the latter acid, in the presence of hot mineral acid, would of course lose carbon dioxide, giving lævulic acid (XVII). Actually lævulic acid was the sole product, whence it follows that the addition of methyl alcohol must have taken place to structure (IV), and not to structure (IVa), which, as other experiments also have shown, is evidently absent from the mobile system.

$$ CH_3 \cdot CH \begin{smallmatrix} CO \cdot CO_2H \\ CH_2 \cdot CO_2H \end{smallmatrix} \quad CH_3 \cdot CO \begin{smallmatrix} CH \cdot CO_2H \\ CH_2 \cdot CO_2H \end{smallmatrix} \quad CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H $$
$$ (\text{XV.}) \qquad\qquad (\text{XVI.}) \qquad\qquad (\text{XVII.}) $$
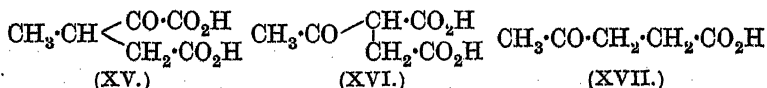
*The Three Stereoisomeric 3-Methyl*cyclo*propane-1 : 2-dicarboxylic Acids.*

In a previous paper of this series these three stereoisomeric acids are described * and their configurations determined. The configurations and m. p.'s are as follows (J., 1923, **123**, 3342) :

trans, m. p. 195°.   trans-cis, m. p. 147°.†   cis-cis, m. p. 108°.
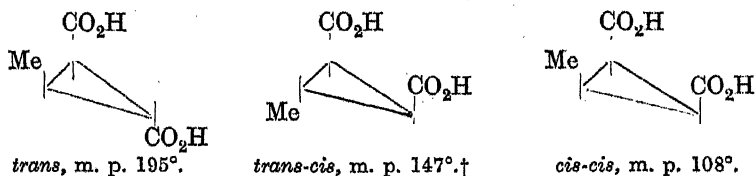
* The isomeride, m. p. 108°, had previously been obtained by Preiswerk (*Ber.*, 1903, **36**, 1085).

† This m. p., previously given as 132°, is depressed to an extraordinary degree by traces of water which are analytically inappreciable—a fact which Feist also noticed. After crystallisation from water, prolonged drying is required to raise the m. p. to its limiting and constant value, 147°.

All three acids were investigated in considerable detail and the structures assigned are, we believe, correct.

Feist was apparently in ignorance of this work when he ascribed (*loc. cit.*) the above three formulæ to three acids (not all of them identical with ours) which he had obtained by reduction either of the *cyclo*propene acid or of its dibromide. Postulating a *cyclo*propane structure in each case, Feist assigned configurations by following a certain very questionable line of reasoning based on the supposed difference between the dibromides of the pure and impure *cyclo*propene acids, which we have shown to be identical; and it is not surprising that from these false premises erroneous conclusions should have been drawn, which, unless corrected, are likely to lead to much confusion.

The only one of Feist's three acids the composition and basicity of which were determined is that having m. p. 147°. There can be little doubt but that this is identical with ours and has the " *trans-cis* "-configuration as indicated in the formula above.* The second acid, m. p. 94°, was not even analysed, but Feist boldly assumed its identity with Preiswerk's acid, m. p. 108°. The third acid, m. p. 138—140°, was analysed, but its basicity was not determined. It seems, therefore, at least probable that either or both of these last two acids have some different constitution; for the last, especially, a lactonic structure, such as $CHMe < {}^{CH(CO_2H)\cdot O}_{CH_2 \underline{\quad\quad} CO}$ (two isomeric forms), is obviously possible.

<div align="center">EXPERIMENTAL.</div>

Optically Active Normal and Labile Ethyl Esters of 3-*Methyl-*Δ^2-*cyclopropene-*1 : 2-*dicarboxylic Acid.*—The object of these experiments was to demonstrate the optical activity rather than to obtain numerical data for the rotatory powers, and the products were therefore not crystallised to constant rotation, as this was found to be very wasteful of material. The racemic acid was resolved by means of quinine and brucine, the alkaloids recommended by Feist (*loc. cit.*), the former being the more convenient for the preparation of the dextro-modification, and the latter for the preparation of the lævo-form. The acids, the rotations of which in alcoholic solution are given below, were then converted into their silver salts, from which, by digestion with ethyl iodide, the active normal esters were produced.

That these active esters actually belong to the normal series and contain no labile isomerides was proved by recombining the dextro- and lævo-modifications to produce the racemic compound.

* Feist assigned the " *trans* "-configuration.

The active preparations, the rotations of which are given below, both melted at 55—56°. The inactive substance produced by their admixture had m. p. 38—39°, and did not lower the m. p. (also 38—39°) of an authentic specimen of the racemic normal ester.

The active normal esters, on distillation under ordinary pressure, yielded optically active, labile esters, which were proved to belong to the labile series, and to contain no trace of normal isomerides, by submitting them to the sodium ethoxide separation previously described (Goss, Ingold, and Thorpe, J., 1923, **123**, 351, method No. 3).

The following rotations were taken in alcoholic solution at 19° :

	Dextro.	Lævo.
Acid.....................................	$[M]_D^{19°} = + 116°$	$[M]_D^{19°} = - 128°$
normal Ethyl ester	$,, = + 213$	$,, = - 221$
labile Ethyl ester	$,, = + 46$	$,, = - 42$

Methyl Hydrogen, Ethyl Hydrogen, and Methyl Ethyl 3-Methyl-Δ^2-cyclopropene-1 : 2-dicarboxylates.

In a static unsymmetrically constituted dibasic acid the carboxyl group most sterically protected in esterification is also the one most protected when the neutral ester is hydrolysed; hence partial hydrolysis and partial esterification lead to isomeric acid esters. In this case, however, the products obtained by these two methods proved to be identical.

The Methyl Hydrogen Ester.—(a) *By hydrolysis.* A solution of the normal dimethyl ester (2·8 g.) in 25 c.c. of 0·66N-methyl-alcoholic potassium hydroxide was left at the ordinary temperature for 15 hours, and the mixture poured into water and extracted with ether. On evaporation of the dried ethereal extract a small amount of neutral ester was recovered. The aqueous solution was acidified and again extracted, and the residue obtained on evaporation of the ether distilled under diminished pressure. The acid ester boiled at 169°/20 mm. and after crystallisation from ligroin was obtained in needles, m. p. 65° (Found : C = 53·6; H = 5·2; M, by titration, = 156. $C_7H_8O_4$ requires C = 53·8; H = 5·2%; M = 156).

(b) *By esterification.* The acid was esterified by passing methyl alcohol vapour through a solution of the acid in methyl alcohol slightly acidified by sulphuric acid, and the acid-ester separated from the neutral ester by means of ether and aqueous sodium carbonate. It was purified like the acid-ester above described, with which it was in every respect identical.

The Ethyl Hydrogen Ester.—This was prepared by partial hydrolysis exactly as described above, excepting that 3·25 g. were

used in place of 2·8 g. The product had b. p. 174°/20 mm. and m. p. 57° (Found : C = 56·4; H = 5·9; M, by titration, = 170. $C_8H_{10}O_4$ requires C = 56·4; H = 5·9%; M = 170).

The Methyl Ethyl Ester.—(a) *From the methyl hydrogen ester.* The acid methyl ester was first converted into its silver salt by the action of silver nitrate on a concentrated aqueous solution of the ammonium salt (the salt is rather soluble in water). The salt was digested for 2 days with an ethereal solution of ethyl iodide, and the ester isolated in the usual way and distilled. It had b. p. 130°/20 mm., but did not crystallise.

(b) *From the ethyl hydrogen ester.* This experiment was carried out in the same way using methyl iodide. The product appeared in every way identical with the previous one, but could not be crystallised (Found : C = 58·7; H = 6·6. $C_9H_{12}O_4$ requires C = 58·7; H = 6·6%).

*Methyl Ethyl 2 : 3-Dibromo-3-methyl*cyclo*propane-1 : 2-dicarboxylate.*—The methyl ethyl cyclopropene ester was treated with the theoretical amount of bromine in chloroform solution. After keeping over-night, the solvent was evaporated and the residue distilled, when the dibromide passed over at 182°/20 mm. (Found : C = 31·6; H = 3·2. $C_9H_{12}O_4Br_2$ requires C = 31·4; H = 3·5%).

*Constitution of 3-Methoxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic Acid* (XIV).

The acid was prepared as described previously (J., 1923, **123,** 3358), using 2N-alcoholic potassium hydroxide for the hydrolysis of its methyl hydrogen and dimethyl esters. Its *cis*-structure was proved by converting it into an anhydride, and the position of the methoxy-group determined, as described in the introduction, by ring-fission to lævulic acid.

The *anhydride,* CMe(OMe) $<\!\!{\underset{\text{CH·CO}}{\overset{\text{CH·CO}}{}}}\!\!>$O, was produced by boiling the acid for 6 hours with 20 times its weight of acetyl chloride. After removing the acetyl chloride and acetic acid by exposure over potassium hydroxide, the anhydride was crystallised from pure acetyl chloride, from which pearly leaflets separated, m. p. 94° (Found : C = 54·0; H = 5·0. $C_7H_8O_4$ requires C = 53·8; H = 5·2%). That no change of configuration occurs during this reaction is shown by the fact that on rehydration with water the original acid is regenerated.

Lævulic Acid (XVII).—The acid was boiled for 2 hours with 20% hydrochloric acid, and the solution then evaporated. The residue had all the properties of lævulic acid, with which it was identified by conversion into its semicarbazone, m. p. 191—192°

(Found : C = 42·2 ; H = 6·2. Calc., C = 41·6 ; H = 6·4%), and phenylhydrazone, m. p. 107—108°. The mixed m. p. of these derivatives with the same substances prepared from authentic lævulic acid showed no depressions.

We desire to thank the Chemical Society for a grant in aid of this investigation.

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　　SOUTH KENSINGTON.　　　　　[Received, December 11th, 1924.]

LXVII.—*The Correlation of Additive Reactions with Tautomeric Change. Part IV. The Effect of Polar Conditions on Reversibility.*

By EDITH HILDA INGOLD (USHERWOOD).

FROM the existence of certain apparent exceptions to Michael's " positive-negative " rule for the direction taken by Michael's addition reaction, the conclusion may be drawn that, in a theoretical sense at least, the addition can take place in both directions to an unsymmetrical, unsaturated ester, although, no doubt, one type of addition will generally be favoured to the practical exclusion of the other.

This inference has an important bearing on the analysis, commenced in Part II (J., 1924, **125**, 435), of the conditions regulating the tendency of carbon chains to break down by retrograde, additive processes, for if the Michael addition can occur in two directions, then two retrograde reactions must be taken into account, and therefore the number of structures susceptible to disruption is multiplied.

For this reason a series of experiments was instituted to ascertain whether the retrograde reaction corresponding with addition in the opposite direction to that given by the " positive-negative " rule could occur ; and, if so, whether the difficulty attending addition in a non-favoured direction would have its counterpart in ease, or in difficulty, of decomposition. If the first of these alternatives be correct, polar influences should inhibit addition in an adverse direction by throwing the *equilibrium* towards the direction favouring the simple molecules, whereas if the second alternative be the true one, difficulty of addition corresponding with difficulty of decomposition, then the adverse polar influences must act by lowering the *velocity* of the reaction in both directions, without notably altering the equilibrium.

The experiments now described prove conclusively (a) that the retrograde reaction corresponding with an abnormal direction of addition can occur; (b) that difficulty of addition in a direction against the polar influence has its counterpart in *difficulty* of disruption.

The decision of the latter point enables the following general principle to be advanced : *The primary effect of polar conditions is on the velocity of reversible additions and not on the equilibrium.*

The investigation described in Part II, of the influence of spatial factors on the reversibility of aldol additions, and that of C. K. Ingold, Perren, and Powell (J., 1921, **119**, 1582, 1976) on the same effect in relation to the Michael addition, lead to a second and complementary generalisation : *The primary effect of spatial conditions is on the equilibrium in reversible additions.* It may be hoped that the application of these two principles will aid the sorting out of the superimposed polar and spatial influences which regulate organic reactions, and are often docketed together as manifestations of " steric hindrance."

A suitable example for study appeared to be provided by the following series of changes (Bone and Sprankling, J., 1899, **85**, 839; and others) :

$CO_2Et \cdot CBrMe_2$ (I.) and	Normal (succinic) type.	Abnormal (glutaric) type.
Ethyl sodiocyanoacetate	$CO_2Et \cdot CMe_2 \cdot CH(CN) \cdot CO_2Et$ (II.)	None formed.
„ sodiomalonate	$CO_2Et \cdot CMe_2 \cdot CH(CO_2Et)_2$ (III.)	$CO_2Et \cdot CHMe \cdot CH_2 \cdot CH(CO_2Et)_2$ (IV.)
„ sodiomethylmalonate	traces only formed.	$CO_2Et \cdot CHMe \cdot CH_2 \cdot CMe(CO_2Et)_2$ (V.)

Now in any of these cases the abnormal product (glutaric type) might conceivably be produced by the recombination of two esters formed from the normal product (succinic type) by a retrograde Michael reaction corresponding with the less usual direction of addition :

$$\text{(III.)} \quad \rightleftharpoons \quad CO_2Et \cdot CMe \vcentcolon CH_2 + CHMe(CO_2Et)_2 \quad \rightleftharpoons \quad \text{(IV.)}$$
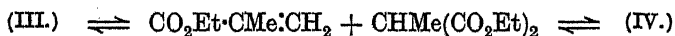
Moreover, if (according to one of the alternative hypotheses) the primary effect of polar conditions is on the equilibrium, these changes should occur under the conditions of the original condensations. Experiment showed, however, that this is not the case, so that the hypothesis of an altered equilibrium is untenable.

At higher temperatures, however, a definite retrograde reaction could be detected of the type corresponding to abnormal direction of addition, although the velocity of the change was very small. The succinic ester (III), which cannot be separated from its glutaric isomeride (IV) and has not previously been obtained in a pure condition, was prepared and examined for purity in the following way. The cyano-ester (II), which on hydrolysis by acids yielded the dibasic acid (VII), was converted by concentrated alkalis into

the tribasic acid (VI). A portion of this was converted into the silver salt and thence into the ester (III). Another portion of the same specimen was heated above its melting point to give the dibasic acid (VII), and a portion of the triethyl ester was hydrolysed by acids to the same dibasic acid. The dibasic acid obtained in these ways was crystallised in fractions, a process which would rapidly concentrate the very soluble α-methylglutaric acid (VIII), if present, in the ultimate residues, which nevertheless proved to be pure dimethylsuccinic acid (VII):

$$\begin{array}{ccc} \text{CMe}_2\text{·CO}_2\text{H} & \text{CMe}_2\text{·CO}_2\text{H} & \text{CH}_2\!\!<^{\text{CHMe·CO}_2\text{H}}_{\text{CHMe·CO}_2\text{H}} \\ \text{CH(CO}_2\text{H)}_2 & \text{CH}_2\text{·CO}_2\text{H} & \\ \text{(VI.)} & \text{(VII.)} & \text{(VIII.)} \end{array}$$
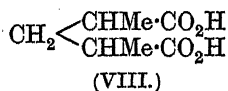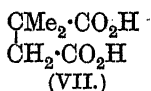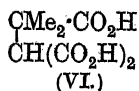
A second portion of the same specimen of triethyl ester was then converted into its sodio-derivative and heated in alcoholic solution for different lengths of time as described in the experimental portion; the regenerated ester was hydrolysed with acids, when, besides much *as*-dimethylsuccinic acid, a small amount of α-methylglutaric acid was obtained. The production of this acid from the recovered ester became appreciable after one week's heating at 100°. A corresponding series of experiments with the cyano-ester (II) yielded purely negative results, and this is in agreement with the known smaller tendency towards the elimination of ethyl cyanoacetate than towards the elimination of ethyl malonate, by a retrograde Michael reaction (C. K. Ingold and Perren, *loc. cit.*).

In contrast with the difficulty attending disruption of the type corresponding with addition in the resisted direction, disruption corresponding with facile normal addition took place with ease. In the case of the glutaric ester (V), which is formed from, and, to a small extent, decomposed into α-methylacrylic ester and methylmalonic ester, the comparatively large speed of decomposition was observed in the following way. If the reversible decomposition of the ester (V) is carried out in the presence of an added substance, such as ethyl cyanoacetate, which can combine reversibly with one of the products, two competing equilibria will be set up:

(V.) $(\text{CO}_2\text{Et})_2\text{CMe·CH}_2\text{·CHMe·CO}_2\text{Et}$ $\rightleftharpoons$
(IX.) $\text{CO}_2\text{Et·CH(CN)·CH}_2\text{·CHMe·CO}_2\text{Et}$ $\rightleftharpoons$

$$\left.\begin{array}{l} (\text{CO}_2\text{Et})_2\text{CHMe} + \\ \text{CO}_2\text{Et·CH}_2\text{·CN} + \end{array}\right\}\text{CH}_2\text{:CMe·CO}_2\text{Et}$$
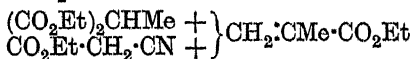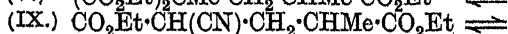
From the second of the two principles given on page 470 it follows that, even if the addition product (V) is greatly favoured by the first of the above equilibria, the addition product (IX) will be even more strongly favoured by the second equilibrium, this ester having fewer (and smaller) substituents at its point of rupture.

Hence, however unfavourable for observing the rate of decom-
position of the ester (V) the original equilibrium might be, it should
be possible, by thus diverting the back reaction into another channel,
to carry the decomposition a considerable distance, and thus observe
its velocity.   A lower limit to the measure of its progress is given
by the rate of formation of the ester (IX).   The mixtures of the
esters (V) and (IX), obtained after heating for different lengths of
time, can readily be isolated and analysed, or hydrolysed to the
glutaric acids and these separated.

From these experiments it is evident that whereas Michael
additions of the type :

$$>C:\overset{|}{C}\cdot CO_2R + HX = >CX\cdot\overset{|}{C}H\cdot CO_2R$$
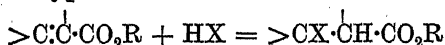
[X equals $CH(CO_2Et)_2$ or a similar group] easily take place, and
are as easily reversed, additions

$$>C:\overset{|}{C}\cdot CO_2R + HX = >CH\cdot\overset{|}{C}X\cdot CO_2R$$
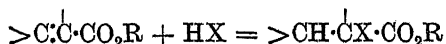
occur, and are reversed, with difficulty or not at all.   The directing
influence of the polar group $-CO_2R$ is therefore primarily exerted
on the velocity, and is similar for both directions of the change.
The bearing of this result on the problem of steric inhibition will
be the subject of a future communication.

EXPERIMENTAL.

Preparation and Stability of Ethyl as-*Dimethylcarboxysuccinate* (III)
and Ethyl as-*Dimethylcyanosuccinate* (II).

A mixture of ethyl as-dimethylcarboxysuccinate and ethyl
α-methyl-α'-carboxyglutarate is formed (Bone and Sprankling,
loc. cit.) by the action of ethyl sodiomalonate on ethyl α-bromo*iso*-
butyrate; but as the isomeric esters cannot be separated it was
necessary to evolve another method for the preparation of the
former.

Ethyl as-*dimethylcyanosuccinate* (II) was prepared from ethyl sodio-
cyanoacetate and ethyl α-bromo*iso*butyrate by Bone and Sprankling's
method (*loc. cit.*), and its purity was proved by converting a
portion of the specimen, by hydrolysis with concentrated hydro-
chloric acid, into as-dimethylsuccinic acid alone, fractional crystal-
lisation from hydrochloric acid failing to reveal the presence of any
α-methylglutaric acid.   (In a similar manner was proved the
absence of this acid in the two specimens of as-dimethylsuccinic
acid mentioned below.*)

* It was proved by special experiments that the presence of small
quantities of α-methylglutaric acid in specimens of as-dimethylsuccinic acid
is easily detected by this means, owing to the large difference in solubility
and m. p.

as-*Dimethylcarboxysuccinic Acid* (VI).—The preceding ester (25 g.) was boiled with 110 c.c. of aqueous potassium hydroxide (3 parts KOH : 4 parts H_2O) for 24 hours, another 20 g. of potassium hydroxide were then added, and the boiling was continued until no more ammonia was given off (about 50 hours). The cooled, cautiously acidified liquid on extraction with much ether gave an acid (yield almost theoretical), m. p. 164—166° (decomp.); 166—167° (decomp.) after crystallisation from ether–chloroform (Found : C = 44·4; H = 5·5; M = 192. $C_7H_{10}O_6$ requires C = 44·2; H = 5·3%; M = 190). The acid forms minute prisms which are very soluble in water, moderately so in ether, and sparingly soluble in chloroform. On heating to 170° in a sulphuric acid bath, the acid is smoothly converted into as-dimethylsuccinic acid and carbon dioxide.

Ethyl as-*Dimethylcarboxysuccinate* (III).—The silver salt, prepared from the tribasic acid (9·5 g.), carbonate-free sodium hydroxide (3 mols.; prepared from sodium), and excess of concentrated silver nitrate solution, was washed with water, alcohol, and ether, and thoroughly dried. A suspension of the dry salt (52 g.) in 500 c.c. of dry ether was gently heated with 60 g. of ethyl iodide on the steam-bath for 3·5 hours, the silver iodide filtered off after 2 days and thoroughly washed with dry ether. From the combined filtrate and washings a residue was obtained which, twice distilled, gave 16 g. of the ester, b. p. 158—165°/22 mm. (Found : C = 56·5; H = 7·9. $C_{13}H_{22}O_6$ requires C = 56·9; H = 8·0%). On hydrolysis with hydrochloric acid as-dimethylsuccinic acid was produced.

Action of Sodium Ethoxide on Ethyl as-*Dimethylcarboxysuccinate*, (a) *at* 78°.—The ester (13·6 g.) was heated for 19 hours with alcoholic sodium ethoxide (1·15 g. of sodium; 14 g. of alcohol), the mixture poured into water, extracted with ether, and the ethereal solution dried and evaporated. The residue was hydrolysed with boiling 20% hydrochloric acid. On cooling, a considerable quantity of pure as-dimethylsuccinic acid crystallised, and the mother-liquors, on evaporating by fractions and finally to dryness, yielded successive crops of the same pure acid unaccompanied by any α-methylglutaric acid.

(b) *At* 100°.—In a similar experiment, carried out in a closed vessel at 100° for 170 hours, a mixture of neutral and acid esters was obtained. These were separated in the usual way with ether and sodium carbonate and hydrolysed by hydrochloric acid to the dibasic acids, which were fractionally crystallised in the manner previously described, yielding, in addition to much as-dimethylsuccinic acid, more soluble and more fusible fractions consisting essentially of α-methylglutaric acid, but in quantity insufficient for

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complete separation by this method from the succinic isomeride. The crude product of a hydrolysis was therefore crystallised from hydrochloric acid in order to separate as much as-dimethylsuccinic acid as possible; boiling with 25% calcium chloride solution, after the mother-liquors had been made alkaline with ammonia, yielded crystals of calcium as-dimethylsuccinate; the filtrate from this was acidified and extracted with a large bulk of ether; from the dried extract a gum was obtained, which solidified (m. p. 67—72°) in a desiccator, and on crystallising from benzene and from hydrochloric acid yielded α-methylglutaric acid,* m. p. 75—76° (Found : $M = 148$. Calc., $M = 146$).

Action of Sodium Ethoxide on Ethyl as-*Dimethylcyanosuccinate.*— In a similar experiment with ethyl as-dimethylcyanosuccinate (period of heating 150 hours), no α-methylglutaric acid could be detected in the hydrolysis products.

Stability of Ethyl αα'-*Dimethyl-α-carboxyglutarate.*—The ester, b. p. 165—170°/21 mm., prepared from ethyl methylmalonate and ethyl α-bromoisobutyrate by Bone and Sprankling's method (loc. cit), was added (58 g.) to an alcoholic suspension of ethyl sodiocyanoacetate, prepared from 22·4 g. of ethyl cyanoacetate, 56 g. of alcohol, and 4·6 g. of sodium. The mixture was heated in a sealed tube at 100° for 18 hours, poured into water, acidified, and extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate solution, and water, and dried with calcium chloride. The residue after evaporation of the ether was distilled, when the main fraction passed over at 165—170°/21 mm. The percentage of nitrogen (2·3) showed that 38% of the ethyl αα'-dimethyl-α-carboxyglutarate had been converted into ethyl α'-methyl-α-cyanoglutarate.

The more volatile fractions (11 g.), b. p. 40—120°/21 mm., were treated with alcoholic sodium ethoxide (prepared from 2·2 g. of sodium), and the whole was poured into water. The methylmalonic ester, which is reprecipitated unchanged by this treatment, was extracted with ether, and digested with concentrated aqueous ammonia, when methylmalonamide* separated (m. p. 208—209°).

The fraction (26·2 g.), b. p. 165—170°/21 mm., obtained in the previous experiment, was mixed with alcoholic ethyl sodiocyanoacetate (prepared from 10·3 g. of ethyl cyanoacetate, 2·0 g. of sodium, and 25 g. of alcohol) and heated in a sealed tube at 100° for 170 hours. On pouring into water and extracting as before, a principal fraction was obtained, b. p. 166—170°/21 mm. (Found : $N = 4·9\%$. For the fraction b. p. 140—165°/21 mm., found $N = 3·1\%$).

* Identified by direct comparison and a mixed m. p. determination.

α-*Methylglutaric Acid.*—The ester (4·6 g.), b. p. 166—170°/21 mm., was hydrolysed by boiling with 30 c.c. of 20% hydrochloric acid, and the product was fractionally crystallised from this solvent. The first fraction contained a large proportion of the two forms of αα′-dimethylglutaric acid. The second fraction, after crystallisation first from benzene containing a little ether and then from hydrochloric acid, yielded α-methylglutaric acid,* m. p. 75—76° (Found : C = 49·0; H = 7·1. Calc., C = 49·3; H = 6·9%).

LXVIII.—*The Mechanism of Kolbe's Electrosynthesis.*

By RALPH EDWARD GIBSON.

IT has long been known that when the salts of certain organic acids are electrolysed under definite conditions in aqueous solution, hydrocarbons, esters, unsaturated hydrocarbons, alcohols, and aldehydes are formed at the anode in proportions differing with the conditions of the experiment.

To account for these reactions, several theories have been advanced (Kolbe, *Annalen*, 1849, 69, 279; Crum Brown and Walker, *ibid.*, 1891, 261, 107; Jahn, *Wied. Ann.*, 1889, 37, 420; Bunge, *J. Russ. Chem. Soc.*, 1890, 21, 525; Kekulé, *Annalen*, 1864, 131, 79; Loeb, *Z. Elektrochem.*, 1896, 3, 43; Schall, *ibid.*, p. 83; Murray, J., 1892, 61, 10; Foerster and Piguet, *Z. Elektrochem.*, 1904, 10, 727; Hofer and Moest, *ibid.*, p. 833; Fichter and Krummenacher, *Helv. Chim. Acta*, 1918, 1, 146; Fichter, Fritsch, and Müller, *ibid.*, 1923, 6, 502), which on close examination prove to be modifications or amplifications of two distinct ideas :

(*a*) That the process is one of direct oxidation (the word is used in the restricted sense of denoting the direct action of oxygen on a molecule or residue), the oxidising agent being the oxygen developed at the anode. This was advanced by Kolbe in 1832.

(*b*) That the various products are the result of direct union of the residues of discharged anions, an hypothesis which was proposed by Crum Brown and Walker some sixty years later.

These two fundamental ideas will be referred to hereinafter as

* Identified by direct comparison and a mixed m. p. determination.

R* 2

the Oxidation Theory and the Discharged Ion Theory of Electro-synthesis. Thus the most important reactions of this field are represented by the two theories as follows :

(a) $R \cdot CO \cdot OH + R' \cdot CO \cdot OH + O = R \cdot R' + 2CO_2 + H_2O$
(Hydrocarbon)

$R \cdot CO \cdot OH + R' \cdot CO \cdot OH + O = R \cdot CO \cdot OR' + CO_2 + H_2O$
(Ester)

$R \cdot CO \cdot OH + O \qquad = ROH + CO_2$ (Alcohol)

(b) $R \cdot CO \cdot O \cdot + R' \cdot CO \cdot O \cdot \qquad = R \cdot R' + 2CO_2$ (Hydrocarbon)

$R \cdot CO \cdot O \cdot + R' \cdot CO \cdot O \cdot \qquad = R \cdot CO \cdot OR' + CO_2$ (Ester)

$R \cdot CO \cdot O \cdot + OH \qquad = ROH + CO_2$ (Alcohol)
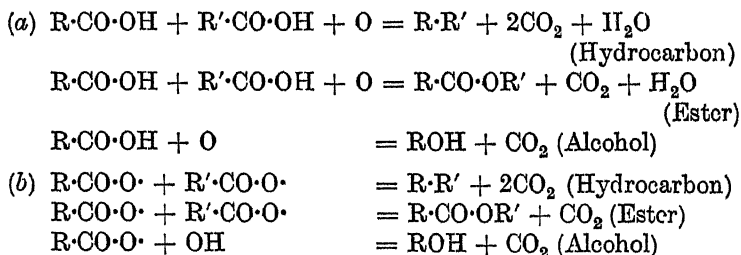
It will be seen that both theories are capable of accounting in a simple and adequate manner for most of the known electrosynthetic and allied reactions and that no evidence on one side or the other can be gathered from qualitative or quantitative studies of the reaction products.

In a former paper (Gibson, *Proc. Roy. Soc. Edin.*, 1924, 44, 140) it was shown that the oxidation theory possessed certain advantages over the discharged-ion theory in the consideration of the behaviour at the anode of mixtures of electrolytes containing as chief constituent one or more fatty acids. It is the purpose of this paper to show that in other cases the oxidation theory, as originally advanced by Kolbe, does account for the observed facts more completely than does the discharged-ion theory.

The strongest argument against the oxidation theory was that emphasised by Murray (*loc. cit.*), namely, the great resistance of fatty acids towards oxidising agents. Murray showed that when a solution of 10% acetic acid and 10% sulphuric acid was electrolysed no appreciable oxidation of the former took place. This argument is, however, no longer valid, for Gordon (*J. Physical Chem.*, 1914, 18, 55) demonstrated that ethane was produced by the oxidation of acetates with persulphates. Presumably the solutions used by Murray were too dilute.

The most conclusive evidence in favour of the oxidation theory, however, was derived from an examination of the electromotive phenomena connected with the initial stages of the electrosynthetic reactions. Preuner and Ludlam (*Z. physikal. Chem.*, 1907, 59, 682) showed that a polished platinum anode in a solution of acetate must acquire a certain definite potential (2·54 volts) before any appreciable amount of ethane is formed and also that at the point, 2·54 volts, on the curve showing the relation between current and anode potential a break (" knickpunkt ") or sharp increase in the gradient is to be observed. This may mean either of two things,

(*a*) that at 2·54 volts the acetate ion is first discharged at the anode, in which case strong evidence in favour of the discharged-ion theory would be obtained, or (*b*) that at 2·54 volts the anode has acquired an oxidising potential high enough to allow the reaction, $2CH_3 \cdot CO \cdot OH + O = CH_3 \cdot CH_3 + CO_2 + H_2O$, to proceed; or, in other words, that at anode potentials above 2·54 volts acetic acid acts as a depolariser. Although it has generally been assumed that interpretation (*a*) is the correct one, this is by no means proved and it was thought that an investigation of the behaviour of the electrolyte and anode in the neighbourhood of this critical point would throw some light on the problem under consideration.

The particular reaction studied in this work was the production of trichloromethyl trichloroacetate by the electrolysis of a solution of trichloroacetic acid (see Elbs and Kratz, *loc. cit.*). This acid was found most convenient for the purpose, as with it the beginning of the electrosynthetic reaction could be visually observed. Strictly speaking, the chief reaction during the electrolysis of this acid is not a synthetic one, for no carbon to carbon union is made, but ester formation is so closely bound up with electrosynthesis that it was considered justifiable to apply deductions from these experiments to cases of true electrosynthesis. The suggestion made by Fichter, Fritsch, and Müller (*loc. cit.*), that the reaction is one in which trichloromethyl alcohol is an intermediate product, appears extremely improbable, when it is considered how unstable this compound is and how comparatively slow the processes of esterification are.

The experiments presently to be described have led to the following conclusions :

(1) That, within wide limits, the process is independent of the current density at the anode.

(2) That a certain definite potential at a polished platinum or iridium anode is necessary and sufficient for the reaction to begin.

(3) That this potential does not represent the discharging potential of the trichloroacetate ion.

(4) That the actual potential of an anode of any metal is not sufficient to cause the reaction, but that the nature and state of the anode also play a large *rôle*; and in this connexion certain peculiarities in the behaviour of platinum anodes have been clearly demonstrated.

(5) That mere electrolytic oxidation of acetic anhydride does not produce ethane as might be supposed from the superoxide theory of Fichter.

EXPERIMENTAL.

Examination of the Behaviour of Anode Potential–Current Curves for Various Anodes in a Normal Solution of Trichloroacetic Acid.— As trichloroacetic acid was reduced at the cathode, it was considered advisable to separate the electrodes as shown in Fig. 1. Sketch (A) shows the normal type of cell used. N is the capillary nozzle of the standard calomel electrode. It was adjustable and could be brought right up against the anode. Sketch (B) illustrates the type used when the anode gases were to be examined.

FIG. 1.
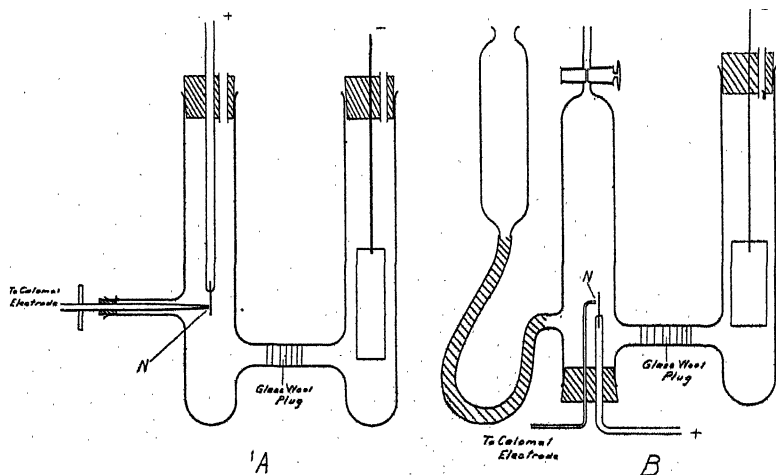
By means of an adjustable potentiometer a variable $E.M.F.$ was applied across the terminals of the cell, and the difference in potential between the anode and the normal calomel electrode was measured by a second potentiometer system with an accuracy of ± 2 millivolts. The polarising current varied far beyond the range of any one instrument, so a series of three ammeters of varying sensitivity was employed, suitable shunting arrangements being provided.

In all cases, except where otherwise stated, a normal solution of trichloroacetic acid was used as electrolyte.

From direct potentiometer readings the potential difference between the anode and a normal calomel electrode was calculated. To obtain the potential of the anode on the hydrogen standard it was necessary to add 0·27 volt to this figure, $+ 0·29$ representing the difference of potential between a normal calomel electrode and a normal hydrogen electrode and $- 0·02$ volt being the boundary

potential at the surface N-KCl/N-CCl$_3$·CO$_2$H, calculated by the formula of Lewis and Sargent (*J. Amer. Chem. Soc.*, 1909, **31**, 363). The results were plotted on graphs with the polarising current (i) as ordinate and the anode potential (V_H) as abscissa. In the curves showing the relation between the logarithm of the current and the anode potential any breaks are much more pronounced than in the ordinary current–potential curves, so in certain cases log i was plotted as ordinate and V_H as abscissa in order to emphasise the presence or absence of breaks.

Preliminary experiments showed that, for a polished platinum anode in N-trichloroacetic acid, there existed a certain critical potential between 2·32 and 2·37 volts. Below this value, gas left the anode as a steady stream of very fine bubbles which rose rapidly from the electrode surface. When, however, the anode potential reached the critical value, the character of gas evolution changed completely. At a comparatively small number of distinct points on the electrode bubbles appeared to grow, some rapidly and some slowly. Each bubble adhered very firmly to the electrode, until, having attained a diameter of 0·5 to 1·5 mm., it rolled slowly to the top of the electrode and was dislodged. Meanwhile, the stream of fine bubbles diminished rapidly and finally ceased. At the points vacated by the large bubbles small crystals of trichloromethyl trichloroacetate were seen and the odour of carbonyl chloride was noticeable in the cell. The conclusion drawn from a large number of experiments was that this change in the appearance of the bubbles of gas could safely be regarded as the criterion of incipient ester formation, for, as long as the gas left the anode as a fine stream, no ester at all was found and no smell of carbonyl chloride observed, but, as soon as the production of large bubbles began, the ester made its appearance.

With anodes of iridium the same phenomenon was noticed and the critical potential was the same as for platinum.

When anodes of gold and of a film of platinum on glass were employed, no change in the character of gas evolution took place even when anode potentials as high as 3 volts were reached. The gas given off at a gold anode working with a current density of 3 amps. per sq. cm. and at a potential of 2·5 volts was analysed and found to be 99% oxygen and to contain no carbon dioxide.

These experiments showed, moreover, that a considerable interval of time was required for the anode to regain equilibrium after each rise in the applied *E.M.F.* In general, with a constant applied *E.M.F.*, the current decreased and the anode potential increased slightly as time went on.

Determination of the Anode Potential–Current Curves for Anodes of Polished Platinum, Gold, and a Platinum Film on Glass.—As the preliminary investigations showed that the point at which the production of trichloromethyl trichloroacetate began was between 2·32 and 2·37 volts, the portions of the curves lying below 1·9 volts, being unnecessary for the present work, were disregarded after it had been seen that there was no discontinuity in the curves in the region from 1—2 volts.

Large platinum electrodes (about 16 sq. cm.) gave very erratic results, which were not improved by stirring the electrolyte or rotating the anode. Consequently a small anode of thin platinum wire, 1 cm. long, was used. It was fitted into the cell and an *E.M.F.* of 2 volts was applied across the terminals. A small current of 0·5—1·0 milliamp. flowed through the cell and the anode acquired a potential of 1·8—1·9 volts. It was allowed to become completely polarised under these conditions for 18—20 hours. Thereafter the applied *E.M.F.* was raised and a series of readings of current and anode potential was taken. After each alteration in the applied *E.M.F.*, time was allowed for the anode to regain equilibrium. During this interval, the current and potential were read every five minutes and from the table so obtained the values at infinite time were found by rough extrapolation. The results from these experiments differed markedly from all previous ones, but were easily reproducible, the curves from four trustworthy experiments resembling each other in every respect. Figure 2 (A) gives a typical result. At 2·10 volts, a sharp break occurred, whereafter the current rose rapidly until a potential of 2·21 volts was reached, when a sudden rise of the anode potential to 2·8—2·9 volts took place and the current decreased. During this increase of potential the critical value was passed and ester formation began. The applied *E.M.F.* was then lowered to a very small value, the current was stopped momentarily, and the anode shaken to remove any adhering ester. A second series of current and anode potential readings was then taken. This time the potential rose rapidly while the current increased slowly. No break at 2·10 volts and no sudden rise of potential were observed, so that it was possible to make an accurate determination of the point at which the bubbles of gas changed in appearance and ester was first formed. The curve was identical with that shown in Fig. 2 (C). The critical point at which ester formation began was found to be between 2·34 and 2·37 volts.

Several experiments were performed in which the anode was first polarised at a potential of 1·9—2·0 volts for 18 hours and then at 2·6—2·9 for 5—10 minutes. Series of readings were there-

after taken as in the previous experiment. The results are given in curves B and C, Fig. 2. Curve B shows the anode in a state intermediate between those represented by A and C. It was observed that in the case of B, and to some extent of C also, the anode potential below 2·2 volts showed a tendency to fall although the applied *E.M.F.* was kept constant. In the experiments the results of which are given by curve C the potential of the anode was not allowed to fall much below 2·2 volts after the preliminary polarisation. The points at which change in the appearance of the bubbles of gas was first noticed and at which the change was complete are shown on this curve.

FIG. 2.

Current–anode potential curves for small anode of polished platinum in
N-trichloroacetic acid. Same anode used in each case.
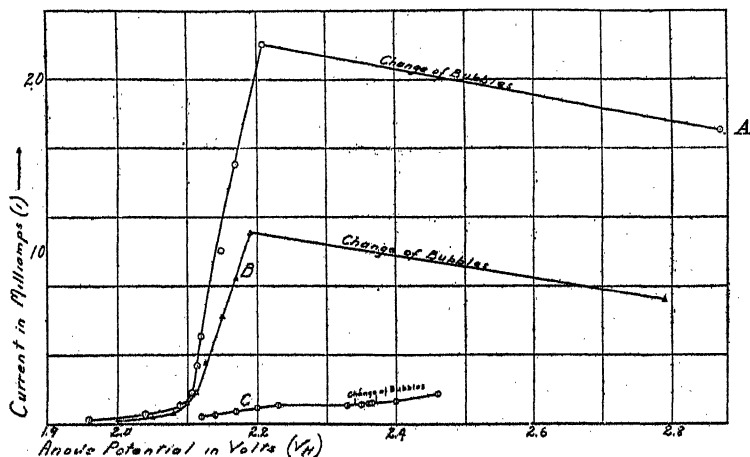
With 2*N*-solutions of trichloroacetic acid curves of an exactly similar type were obtained, whilst in the case of *N*/10-acid, although the curve was exactly the same as Fig. 2 (A), no change in the appearance of the bubbles was observed and no ester was seen, even after prolonged passage of heavy current, which would indicate that the actual formation of ester does not in itself cause the great rise in anode potential already referred to.

A gold anode, 0·5 cm. long and 1 mm. in diameter, was treated in exactly the same way as described on page 480. The results are recorded in Fig. 3. It will be seen that extremely high currents were necessary to produce the anode potentials observed with platinum anodes. In this and the following experiments the electrodes came into equilibrium very quickly after each rise in the applied *E.M.F.* at potentials above 2·2 volts.

A piece of glass tube, closed at one end, was coated with a layer of " Glanzplatin " and ignited, whereby a band of one continuous platinum film on the glass was obtained. The electrode so formed was polarised as already described on page 480. The results are plotted in Fig. 4, the dotted curve representing the logarithm of the current.

FIG. 3.

Current–anode potential curve for small anode of gold in N-trichloroacetic acid
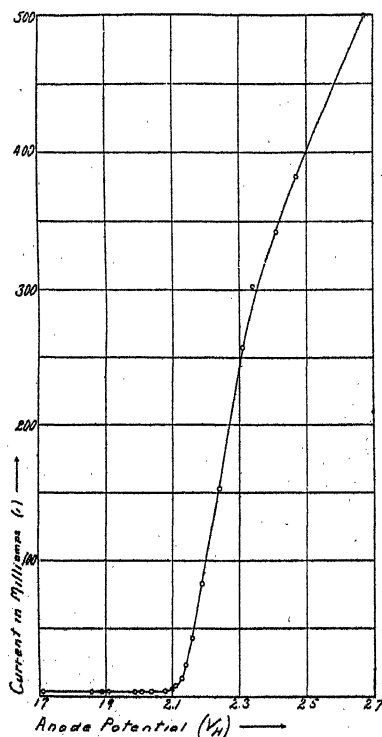
FIG. 4

Current–anode potential curve for anode made of platinum film on glass in N-trichloroacetic acid.
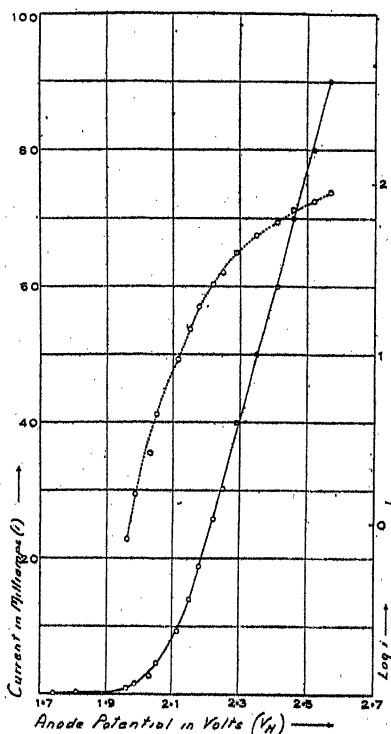
Determination of the Amount of Oxygen evolved in Unit Time above and below the Critical Point.—If the point at 2·35 volts, where ester was first formed, represented merely the discharging potential of the anion, it would be expected that the volume of oxygen evolved in unit time at potentials above this point should be equal to or greater than that evolved at potentials below it, since the effect of the discharge of the trichloroacetate ions should merely be superimposed on and not displace that of the previous discharge of OH or O ions whence the oxygen, evolved below the critical

point, was presumably derived (see Le Blanc, "Text-book of Electro-chemistry," trans. by Whitney and Brown, New York, 1907, p. 303). If, on the other hand, this point marks the start of oxidising processes, it would be expected that considerably less oxygen per unit time would be evolved after the beginning of the process. The cell illustrated in Fig. 1 (B) was used. A current of 0·5 milliamp. was passed through the electrolyte for 18 hours prior to the experiment, so that the electrode might be completely polarised and the solution saturated with oxygen. The current was then adjusted so that the anode potential was just below 2·33 volts. The gas produced was collected and analysed, the current and potential being read and adjusted every five minutes. Thereafter the applied $E.M.F.$ was raised until complete change in the appearance of the bubbles on the anode had taken place. The current was passed for some time in order to saturate the solution with carbon dioxide and to expel any oxygen. The sample of gas was then collected. Table I gives the results from several experiments with N- and $2N$-solutions of trichloroacetic acid and shows quite definitely that oxidation processes do take place.

TABLE I.

Electrolyte.	Average current. Amp.	Anode potential. Volts.	Oxygen per amp.-hour. C.c.	Oxygen per hour. C.c.
	0·014	2·13—2·17	203	2·8
	0·013	2·17—2·24	213	2·8
$N\cdot CCl_3\cdot CO_2H$	0·026	2·46—2·8	14	0·4
	0·030	2·46—2·8	13	0·4
$2N\cdot CCl_3\cdot CO_2H$	0·10	1·98	72	0·8
	0·18	2·5 —2·8	17	0·3

The Electrolysis of a Mixture of Sulphuric Acid and Acetic Anhydride.—With a view to test the probability of the hypothesis of Fichter and Krummenacher that ethane is formed as the result of the electrolytic oxidation of acetic anhydride, a mixture of 100 c.c. of acetic anhydride, 20 c.c. of concentrated sulphuric acid, and 5 c.c. of water was electrolysed in a divided cell. The composition of the anode gas was as follows : CO_2, 87; CO, 3; O_2, 9; inflammable residue, 1%. The inflammable residue was found to be methane by determinations of its boiling point and by combustions. 100 C.c. required (a) 208, (b) 200 C.c. O_2. CH_4 requires 200 c.c. No trace of ethane was found.

Discussion of Results.

Fig. 2 shows that for ester formation to begin it is necessary that the anode acquire a potential of 2·35 volts and that the density of the current, apart from producing this potential, do not have any

influence on the reaction. Now the influence of anode current density on the reaction is one of the main supports of the discharged-ion theory, which supposes that, until the concentration of the discharged anions becomes large enough for them to react with each other, they react with the surrounding water, giving oxygen and the original acid, and it is obvious that the concentration of discharged ions is proportional to the current density (see Murray, *loc. cit.*). This theory is, therefore, tenable only if the notion of discharging potentials is accepted, *i.e.*, if we suppose that in the experiments under consideration no trichloroacetic ions are discharged until the anode acquires a potential of 2·35 volts. If this hypothesis be not accepted—and it must be admitted that it has not been very well substantiated—the only possible explanation of the non-formation of ester below 2·35 volts is that the oxidising power of the anode is not sufficient to bring about the reaction, $2CCl_3 \cdot CO \cdot OH + O = CCl_3 \cdot CO \cdot O \cdot CCl_3 + CO_2 + H_2O$, at potentials below this value.

The problem, therefore, resolves itself into ascertaining whether there is any reason to believe that the discharging potential of the trichloroacetate ion is in the neighbourhood of 2·35 volts. The only evidence of the discharging potentials of anions at present available for chemists is that afforded by breaks in the curves showing the relation between current and anode potential for indifferent anodes in a solution containing the anion. An examination of the curves obtained in these experiments reveals no sign of a break about 2·35 volts. This is very well shown in the cases of anodes of gold and of a film of platinum on glass, at which no disturbing processes, such as ester formation, take place. Hence we conclude that the discharging potential of the trichloroacetate ion does not lie near the point at which ester formation begins. Such a conclusion was confirmed by the experiments on the relative compositions of the gases evolved before and after the start of the reaction.

Another interesting result of these experiments is the singular behaviour of platinum anodes evolving oxygen in a solution of trichloroacetic acid. These phenomena are explained as follows : Several authors (Bennett and Thompson, *J. Physical Chem.*, 1916, **20**, 300; Bancroft, *ibid.*, p. 376; *Z. Elektrochem.*, 1899, **6**, 40; Lewis and Jackson, *Z. physikal. Chem.*, 1906, **56**, 207) have attributed the polarisation *E.M.F.* of an anode to the accumulation thereat of active or atomic oxygen. The anode overvoltages of the various metals may then be attributed to their powers of accelerating or retarding the reaction, $O + O = O_2$. As molecular oxygen (O_2) is useless as far as oxidation is concerned, this hypothesis connects in a reasonable way the overvoltage and oxidising power

of an anode.   It would appear from the above results that a platinum electrode, under the conditions of these experiments, is capable of existing in at least two states :

State α, a state of low oxidising power in which the metal accelerates the reaction $O + O = O_2$.

State β, a state of high oxidising power in which the metal retards the reaction $O + O = O_2$.

After being polarised for many hours at a low potential, the metal is brought into state α, so that, on the applied *E.M.F.* being raised, the reaction, $O + O = O_2$, is accelerated and a comparatively low anode potential exists. This is represented by the region 1·9—2·2 volts, Fig. 2 (A and ● When a potential slightly exceeding 2·2 volts is reached, state α becomes unstable and the platinum passes to state β. The amount of oxygen being discharged at the anode then becomes too great for the reaction, $O + O = O_2$, now retarded, to dispose of, so that the anode potential rises to a high value before equilibrium is reached. By being polarised for a short time at a high potential, the anode is brought into state β, which remains metastable below 2·2 volts, so that it is possible to obtain a curve such as 2 (C). That the state β is only metastable at low potentials is shown by what may be termed the transition curve 2 (B), and by the observation, already made, that the anode potentials tend to fall and the current to rise while the applied potential is kept constant below 2·2 volts.

In the case of a film of platinum on glass it appears that state α is extremely stable and that potentials as high as 3·0 volts may be reached without transition to state β taking place at any appreciable rate.   Experiments showed, moreover, that in platinised platinum state α is extremely stable at comparatively high voltages. Preuner and Ludlam (*loc. cit.*), however, have drawn attention to the fact that, when anodes of this material are used with heavy currents for a prolonged period, their potential rises and they pass to the polished or white variety, acquiring at the same time the power of oxidising acetic acid to ethane.   This would indicate that a slow transition from state α to state β takes place.

Conclusion and Summary.

The work of previous investigators appears to give no evidence which directly contradicts the idea that the process of electrosynthesis is an oxidising one, as Kolbe himself imagined.   In this work I have attempted to show that direct evidence in favour of the oxidation theory and antagonistic to the discharged-ion theory has been obtained from an examination of the electromotive

phenomena connected with the beginning of the electrosynthesis or the allied reaction, ester formation, namely, that an anode of platinum or iridium must acquire a certain definite potential before the reaction will proceed and that there are no grounds for believing that this is the discharging potential of the anion in question. It is therefore considered justifiable to formulate the electrosynthetic reactions in the manner first proposed by Kolbe with the necessary additions [equations (a), page 476]. One must admit that these equations are still somewhat vague, but they represent completely our present knowledge of the subject. Although acetic anhydride is vigorously oxidised at a platinum anode, no ethane is produced, a fact which renders improbable theories of this reaction involving the oxidation of anhydrides. There is, in my opinion, no trustworthy foundation for the assumption that anhydrides, peroxides, peracids, or other intermediate compounds are formed (see also Gibson, loc. cit., p. 151).

The formation of ethane by the electrolysis of potassium acetate with a platinum anode is, in reality, a very special case of oxidation, for the oxidising agent possesses three peculiar characteristics :

(1) It is capable of creating and maintaining around itself, under suitable conditions, a large concentration of the appropriate oxidisable material. (This is done by the anode attracting and discharging acetate ions which thereafter react with water, regenerating the acid.)

(2) It is capable of developing very high oxidising powers.

(3) Its zone of action is extremely circumscribed, being limited to the comparatively small surface of the anode.

Thus it is somewhat unfortunate that the discovery of Kolbe preceded that of Hofer and Moest, for alcohol formation from fatty acids might well be regarded as the normal electrolytic oxidation reaction, the abnormal ethane formation taking place only when conditions, such as almost entire absence of other anions, are favourable to the building of large concentrations of the organic acid at the anode. The third characteristic shows how it is possible for easily oxidisable, non-ionised substances, such as alcohols and aldehydes, to appear among the end products. They are, in a sense, crowded out of the zone of oxidation as soon as formed by the incoming stream of anions and there is no force which tends to attract them back again.

These considerations show that the oxidation theory presents to us a simple and complete account of the various processes occurring at the anode during the electrolysis of salts of organic acids and offers a key to the solution of what have hitherto been regarded as somewhat mysterious anode phenomena.

LXIX.—*The Diffusion-potential and Transport Number of Hydrochloric Acid in Concentrated Solution.*

By SYDNEY RAYMOND CARTER and FREDERICK MEASHAM LEA.

As a first approximation, the diffusion potential set up at the boundary between N-hydrochloric acid and similar acid of higher concentration might be calculated from the usual formula

$$(1) \quad \pi = (u - v)/(u + v) \cdot RT/nF \cdot \log c_2/c_1,$$

where u and v are the ionic mobilities. The evaluation of c_1 and c_2, the ionic concentrations, however, is inadmissible in solutions of high concentration, moreover the above formula implies a constant transport number.

The method of Ferguson (*J. Physical Chem.*, 1916, **22**, 326; *J. Amer. Chem. Soc.*, 1921, **43**, 2150) based on a study of concentration cells of the following types was employed.

A. Cell with transport.

$$(Pt)H_2 \,|\, HCl(c_2) \,|\, HCl(c_1) \,|\, H_2(Pt).$$

B. Cell without transport.
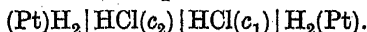
$$(Pt)H_2 \,|\, HCl(c_2), HgCl \,|\, Hg \,|\, HgCl, HCl(c_1) \,|\, H_2(Pt).$$
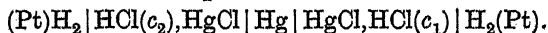
The gas electrodes were at atmospheric pressure, consequently the actual hydrogen pressure in the electrodes is atmospheric less the vapour pressure of the hydrochloric acid in contact with it at that electrode.

The following equations may be deduced from thermodynamical considerations for the *E.M.F.* of these cells :

$$(2) \quad \epsilon = \epsilon' - RT/2F \cdot \log_e (b - c)/(b - c') = 2n_a RT/F \cdot \log_e a'/a.$$
$$(3) \quad E = E' - RT/2F \cdot \log_e (b - c)/(b - c') = 2RT/F \cdot \log_e a'/a.$$

The vapour pressures of the dilute and the concentrated solution are c and c', respectively, the activities of the ions in these solutions are a and a', and b is the barometric pressure. The observed potentials for the cells with and without transport, respectively, are ϵ' and E', whilst ϵ and E are the *E.M.F.*'s after

correction for the inequality in hydrogen pressure at the two electrodes.

These equations are somewhat similar to those deduced by Ferguson, but, in addition, they take into account the vapour pressures of the solutions.

A constant transport number is also assumed, but this is inadmissible over a wide range of concentration, since when two solutions of different concentrations are brought into contact, as they are in cell A, the value of the transport number acting at the liquid junction will not be that which holds in the main bulk of either of the two solutions, but some "mean effective" value (W).

It is given by

(4) $W = $ (equation 2)/(equation 3) $= \epsilon/E$

and equation 2 becomes

(5) $\epsilon = 2W . RT/F . \log a'/a.$

For dilute solutions, in which the transport number does not vary appreciably with concentration, the effective value so obtained will be identical with the ordinary Hittorf transport number. It is, however, of wider application and, since equations 5 and 3 are thus applicable to concentrated solutions even where a constant transport number cannot be assumed, the following modified equation may now be employed.

(6) $\pi = (1 - 2W)RT/F . \log a'/a.$

Finally, by combination of equations 2, 3, 5, and 6, we obtain

(7) $\pi = E'/2 - \epsilon' + RT/4F . \log (b - c)/(b - c').$

This expression for the diffusion potential is valid for strong solutions and contains only terms which can be evaluated by direct measurement.

Previous work on concentration cells of these types was carried out by MacIntosh (*J. Physical Chem.*, 1898, **2**, 273, 427), Dolezalek (*Z. physikal. Chem.*, 1898, **26**, 321), Jahn (*ibid.*, 1911, **33**, 545), Ellis (*J. Amer. Chem. Soc.*, 1916, **38**, 737), Noyes and Ellis (*ibid.*, 1917, **39**, 2532), and Linhart (*ibid.*, 1917, **39**, 2601; 1919, **41**, 1175).

Data are not available, however, for hydrochloric acid at 18° above 4·5N in cells without transport, nor for acid concentration above N in cells with transport.

<center>E X P E R I M E N T A L.</center>

The cells examined were of the types A and B previously given. The dilute hydrochloric acid (concentration c_1) was N in all

cases. The stronger hydrochloric acid solution (concentration c_2) was varied up to $11 \cdot 5N$.

The reversible Hg | HgCl electrodes may be briefly considered. It is essential that the solubility of the depolarising agent at this anodically reversible electrode should be very small compared with the concentration of the electrolyte; otherwise the amount of chlorine ion introduced into the solution by the depolariser dissolving may be sufficient to cause an appreciable change in the concentration of chlorine ion at that electrode. The solubility of mercurous chloride in hydrochloric acid solution has been investigated by Richards and Archibald (*Z. physikal. Chem.*, 1902, **40**, 391). In hydrochloric acid solution, mercurous chloride decomposes to a slight extent into mercury and mercuric chloride, and an equilibrium between these substances is established. The maximum molar ratio [$HgCl_2$]/[HCl] was found by these workers to occur at about $5 \cdot 5N$-acid and was only $0 \cdot 036\%$. Thus there appears to be no real objection to the use of this electrode in concentrated hydrochloric acid solutions. A comparison (see p. 493) of the experimental results, where possible, with those obtained by Dolezalek, who used chlorine gas electrodes, shows agreement and from this the suitability of the calomel electrode is inferred. This point is of some importance, as Dolezalek states that calomel electrodes cannot be used, at 30°, in strong acid solutions.

The calomel electrodes were made up in the usual manner in hydrochloric acid of the required concentration.

Hydrogen Electrodes.—These were of the Wilsmore pattern containing platinised platinum electrodes. These electrodes attained equilibrium in about 45 minutes and were constant to $0 \cdot 0005$ volt, even when the hydrogen supply had been cut off for some time. A bubbler filled with acid of the same concentration as that in the electrode was used in connexion with each hydrogen electrode in order to avoid loss of hydrochloric acid on continued passage of hydrogen through the latter.

Preparation and Measurement of Cells.—The hydrochloric acid in the cells and bubblers was titrated with standard sodium carbonate solution before and after the potential measurements. For acids below about $7 \cdot 0N$ the change in concentration was very small, but at higher concentrations some change occurred, amounting to a maximum decrease of $0 \cdot 15N$ for $11 \cdot 5N$-acid. In the latter cases, the mean value of the initial and the final acid concentration was usually taken.

In the cells with transport, the two hydrochloric acid solutions of different concentrations were connected by means of an inverted U-tube filled with the more dilute solution. The tubes were of

about 3 mm. internal diameter and the ends were plugged with filter-paper. Such an arrangement was found to give diffusion potentials reproducible within fairly narrow limits. Measurements were carried out at 18°.

Results.

A series of concentration cells of the types A and B was measured, the more dilute acid being N in all cases and the stronger acid varying from $1.8N$ to $11.5N$. The potentials, ϵ' and E', are the directly measured values for the cells *with* and *without* transport respectively. The acid concentration given is that of the stronger solution. Concentrations are stated in gram-equivalents per litre.

TABLE I.

[HCl].	ϵ' (volt).	E' (volt).	[HCl].	ϵ' (volt).	E' (volt).
1·776	0·0060	0·0382	7·78	0·0469	0·2368
2·23	0·0100	0·0604	8·38	0·0526	0·2533
3·74	0·0184	0·1129	9·56	0·0619	0·2828
4·62	0·0235	0·1386	10·20	0·0686	0·3004
5·72	0·0304	0·1758	11·32	0·0820	0·3299
6·61	0·0365	0·1990	11·59	0·0842	0·3388

In order to calculate the diffusion potentials by equation (7) from these $E.M.F.$ data, the value of the vapour pressure correction term must be known. The correction term, $RT/4F \cdot \log (b - c)/(b - c')$, has been calculated by the aid of Allen's * data on the vapour pressure of hydrochloric acid (*J. Physical Chem.*, 1898, 2, 120). Below $9N$-acid, the value of this term is negligibly small. The calculated values from $9N$ upwards are tabulated.

TABLE II.

[HCl]	9·0	10·0	11·0	11·5
Correction term (volt)	0·0001	0·0002	0·0004	0·0009

In Table III the smoothed values of ϵ' and E' obtained from the data of Table I are given in columns 2 and 3, and the values of the diffusion potential, π, as calculated from equation (7), in column 4. For the purpose of comparison, the values of the diffusion potential, as calculated from equation (1), using conductivity–viscosity data and assuming a constant transport number, are tabulated in column 5. Column 1 gives the acid concentration in gram-equivalents per litre of the stronger hydrochloric acid

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* These data are for the partial pressure of the hydrogen chloride only. The partial pressure of the water is neglected, since at 18° it is only 15·4 mm. for pure water and diminishes as the concentration of the acid increases. The $E.M.F.$ correction for the difference in partial pressures of the water between two hydrochloric acid solutions of $1N$ and upwards is accordingly very small and therefore has not been considered.

solution, it being understood that the weaker acid solution was always N.

TABLE III.

Observed $E.M.F.$

[HCl].	With transport. ϵ' (volt).	Without transport. E' (volt).	Diffusion potential π (volt).	
			By $E.M.F.$	By conductivity-viscosity data.
2·00	0·0082	0·0490	0·0163	0·0094
3·00	0·0144	0·0880	0·0296	0·0141
4·00	0·0195	0·1190	0·0400	0·0169
5·00	0·0255	0·1520	0·0505	0·0186
6·00	0·0321	0·1825	0·0591	0·0197
7·00	0·0395	0·2138	0·0674	0·0201
8·00	0·0484	0·2420	0·0726	0·0204
9·00	0·0571	0·2630	0·0770	0·0207
10·00	0·0666	0·2940	0·0806	0·0211
11·00	0·0775	0·3220	0·0839	—
11·50	0·0836	0·3360	0·0853	—

The experimental values (column 4) are widely different from those calculated from conductivity–viscosity data (column 5).

The values of the " effective " transport number as defined by equation (4) have been calculated, the values of ϵ' and E' given in Table III being used to calculate the values of ϵ and E (equations 2 and 3). The " effective " transport numbers, W_{Cl}, given in Table IV, represent the " effective " values between N-hydrochloric acid and a second solution of the normality shown.

TABLE IV.

[HCl]	1·00	2·00	3·00	4·00	5·00	6·00	·7·00
W_{Cl}	—	0·16(7)	0·164	0·164	0·168	0·176	0·185
n_a	0·155	0·180	0·200	—	0·238	—	0·292
[HCl]	8·00	9·00	10·00	11·00	11·50		
W_{Cl}	0·200	0·214	0·227	0·242	0·252		

The value for $2·00N$-acid can be regarded only as approximate, owing to the very small potential values from which it was calculated. The ordinary Hittorf transport numbers, n_a, for hydrochloric acid from N to $7N$ (Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1898, p. 201) are given for purposes of comparison. Henderson (Z. physikal. Chem., 1908, 63, 337) gives a value $n_a = 0·17$ for $6N$—$8N$-hydrochloric acid at 30°.

Application to an Oxidation Cell.—As a check on the results obtained, measurements were carried out on oxidation-reduction cells of the following types :

(a) $(Pt)\,|\,CuCl,CuCl_2,xN\text{-}HCl\,|\,N\text{-}HCl\,|\,N\text{-}KCl\,|\,N\text{-}KCl,HgCl\,|\,Hg$.

(b) $(Pt)\,|\,CuCl,CuCl_2,xN\text{-}HCl\,|\,N\text{-}HCl,HgCl\,|\,Hg\rceil$
$Hg\,|\,HgCl,N\text{-}KCl\,|\,N\text{-}KCl\,|\,N\text{-}HCl,HgCl\,|\,Hg\rfloor$

Cell (a) was of the general type on which work had been carried out in another investigation, and by introducing the $HgCl\,|\,Hg\,|\,HgCl$

electrodes across the hydrochloric acid boundary confirmation of the previous results was obtained. The same half-element (Pt) | CuCl,CuCl$_2$,xN-HCl was used for (a) and (b), and the complete cell with calomel half-element was then measured with, and without, the intermediate HgCl | Hg | HgCl electrodes.

If the E.M.F.'s of the cells (a) and (b) be denoted by E_1 and E_2, respectively, then for any given acid concentration, xN, it may easily be shown that $E_2 - E_1 = E - \epsilon$, where E and ϵ represent the E.M.F.'s of the previously considered hydrochloric acid concentration cells without and with transport at the same acid concentration. The results obtained with the two sets of cells measured were : for [HCl] = 9·15 and 6·30, $E_2 - E_1$ = 0·2145 and 0·1577, and $E - \epsilon$ = 0·2135 and 0·1572, respectively. The agreement is satisfactory.

Relation between the E.M.F. *of a Concentration Cell and the Partial Pressure of the Hydrochloric Acid.*—The E.M.F. of a concentration cell without transport may be calculated directly from the partial pressure of one of its constituents by means of Dolezalek's equation (*Z. physikal. Chem.*, 1898, **26**, 321) : $\Delta e = e' - e = RT/nF[\log p'/p + \log (b - p)/(b - p')]$, where e' and e are the E.M.F.'s of the two similar cells containing hydrochloric acid of partial pressure p' and p, respectively, Δe is the observed E.M.F. when the two cells are connected in opposition, and b is the barometric pressure.

The partial pressure of hydrogen chloride, which becomes appreciable in solutions above $8N$ at 18°, has been measured for solutions up to $12N$ by Allan (*loc. cit.*). The values given in column 2 (Table V) have been obtained by inter- and extra-polation of the graph formed by plotting $\log p_{HCl}$ against concentration. The observed E.M.F.'s of the cells without transport, E', in column 3 of Table III refer to N- and xN-hydrochloric acid respectively, consequently the difference in E.M.F. of E represents the value which a concentration cell would show if it contained these concentrations of acid. In this way, the observed value of ΔE (Table V, column 6) has been obtained for several concentrations between $7N$ and $11N$. The differences in hydrogen pressure have been corrected by means of equation (3).

TABLE V.

[HCl].	p_{HCl} in mm. of Hg.	Δe calc.	[HCl].	E obs.	ΔE obs.
{ 11·0 { 10·0	48·98} 17·38}	0·0272	{ 1·0—11·0 { 1·0—10·0	0·3212} 0·2936}	0·0276
{ 11·0 { 8·0	48·98} 2·19}	0·0799	{ 1·0—11·0 { 1·0— 8·0	0·3212} 0·2420}	0·0792
{ 11·0 { 7·0	48·98 0·7586}	0·1066	{ 1·0—11·0 { 1·0— 7·0	0·3212} 0·2138}	0·1074

The agreement between the calculated and the observed values in columns 3 and 6 is satisfactory.

Comparison of Chlorine Gas and Calomel-Mercury as Anodically Reversible Electrodes.—Dolezalek (*loc. cit.*) measured the *E.M.F.* of cells without transport of the type

$$(\text{Pt})\text{H}_2 \,|\, \text{HCl}(c_1) \,|\, \text{Cl}_2(\text{Pt}) \dots \dots (\text{Pt})\text{Cl}_2 \,|\, \text{HCl}(c_2) \,|\, \text{H}_2(\text{Pt})$$

for concentrations of hydrochloric acid varying between $5N$- and $12 \cdot 25N$, and a comparison with the present results is of interest.

In both cases, the difference between the *E.M.F.*'s of any pair of cells gives the *E.M.F.* of a concentration cell without transport for the corresponding concentrations of hydrochloric acid. Dolezalek's Δe for $30°$ is reduced to its value for $18°$ by multiplying by the ratio of the absolute temperatures, $(273 + 18)/(273 + 30)$. The results are set out in Table VI.

TABLE VI.

[HCl].	Dolezalek. $t = 30°$. e.	$t = 30°$. Δe.	$t = 18°$. Δe.	Carter and Lea. $t = 18°$. E'.	$t = 18°$. $\Delta E''$.
5·0N	1·189}			0·1520}	
11·0N	1·008}	0·181	0·174	0·3220}	0·1700
6·0N	1·160}			0·1825}	
11·5N	1·001}	0·159	0·153	0·3360}	0·1535

Since Dolezalek used gas electrodes of chlorine, the close agreement between the values of Δe and $\Delta E'$ for $18°$ further confirms the suitability of Hg|HgCl as an anodically reversible electrode in strong hydrochloric acid.

Summary.

The diffusion potential set up between N-hydrochloric acid and a similar solution of higher concentration, varying from N to $11 \cdot 5N$, has been investigated.

The theoretical considerations underlying the method employed have been outlined.

The potentials of a series of hydrochloric acid concentration cells with, and without, transport have been determined.

The values of the diffusion potentials calculated from the results of these measurements are compared with the values obtained from conductivity–viscosity data.

The " effective " transport numbers have been calculated.

The applicability of Dolezalek's equation for the calculation of the *E.M.F.* of a concentration cell with hydrochloric acid at $18°$ has been confirmed.

The suitability of " calomel-mercury " as an anodically reversible electrode in concentrated hydrochloric acid has been demonstrated.

NOTES.

Reduction of Aromatic Nitro-compounds. By RALPH WINTON WEST.

ON the laboratory scale, considerable difficulty is often experienced in the reduction of aromatic nitro-compounds to the corresponding amines. The difficulty of regulating the energy of the reduction often leads to decomposition of the amine, with the formation of undesirable products. Thus, the main product of the reduction by stannous chloride of *o*-bromonitrobenzene is aniline, whilst a considerable quantity of the free amino-acid is produced in the reduction of ethyl *p*-nitrobenzoate. In other cases, the method of working up the product of the reduction is inconvenient and wasteful; *e.g.*, *m*-dinitrobenzene to *m*-phenylenediamine. The method here described has been•found to give good yields of very pure products.

The nitro-compound (1 g.-mol.) is heated to boiling on the waterbath with methylated spirit (500 c.c.) and concentrated hydrochloric acid (10 c.c.). Iron filings (170 g. for each nitro-group present in the compound) are introduced in four portions, 5 minutes being allowed between each addition. The mixture should be kept at vigorous ebullition in order to prevent the iron from caking, and the heating continued for 2 hours after the final addition of iron. The subsequent treatment of the solution depends on the nature of the amino-compound.

(a) It may be made alkaline with caustic soda (10 g.) and steamdistilled. In this way, the first distillate of alcohol is collected separately from the turbid distillate of the substance.

(b) After addition of alcoholic caustic soda equivalent to the hydrochloric acid employed, the hot liquid is filtered and the residue washed once with spirit. The bulk of the alcohol is removed by distillation, and the hydrochloride of the base precipitated by the addition of concentrated hydrochloric acid.

Nitro-compound.	Reduction product.	Yield %.	Method used.
α-Nitronaphthalene.	α-Naphthylamine.	90	b
o-Bromonitrobenzene.	o-Bromoaniline.	82	a
Ethyl p-nitrobenzoate.	Ethyl p-aminobenzoate.	80	b
m-Dinitrobenzene.	m-Phenylenediamine.	82	b
2 : 4-Dinitrotoluene.	2 : 4-Tolylenediamine.	85	b
p-Nitrophenetole.	p-Aminophenetole	78	b

When less than 0·5 g.-mol. of the nitro-compound is used, the quantity of the hydrochloric acid is reduced to 5 c.c.

Where the hydrochloride of the base is somewhat soluble in concentrated hydrochloric acid, a possible alternative under (b) would be to remove most of the alcohol, saturate with hydrogen chloride, and add ether to precipitate the hydrochloride of the base.—IMPERIAL COLLEGE, S.W. 7. [Received, January 6th, 1925.]

Some Metallic Couples Decomposing Water at the Ordinary Temperature. By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

DURING the course of experiments on the liberation of hydrogen from various reagents by the action of metals, we have observed several instances of metallic couples which readily decompose water at the ordinary temperature with the evolution of hydrogen. We are of opinion that some of these may be found of service in reduction processes, for example, in the reduction of organic substances where it is necessary to preserve a neutral medium.

In the experiments which follow, magnesium sheet (1 sq. cm.) was cleaned with hydrochloric acid and placed in 5 c.c. of a 2% solution of ammonium chloride containing a small quantity of the chloride of the metal to be reduced. After the vigorous reaction had set in, the couple was well washed and then put into 100 c.c. of water. The magnesium–copper couple produced when the ammonium chloride contained 0·2% of cupric chloride was remarkably active towards water. The reduced metal formed a black, closely adherent film, quite unlike the spongy copper reduced from an acid solution of the chloride. The most active couples were produced by placing magnesium in a 2% solution of ammonium chloride to which was added 0·2% of crystallised nickel chloride, ferrous sulphate, or cobalt chloride. In these cases also, the deposits were of very fine texture and firmly adhered to the magnesium, and this probably accounts for the increased activity over couples prepared by other methods. These couples, when placed in water, at first produced a vigorous decomposition, which, after a few minutes, subsided to a steady slow evolution of hydrogen continuing for several hours. If the conditions of reaction permit

of the addition of 0·1% of ammonium chloride, the life of the couple is greatly prolonged. Couples of magnesium with platinum or gold, produced by adding to the ammonium chloride 0·02% of auric chloride or platinum chloride, were not very active except on warming.—THE UNIVERSITY OF MANCHESTER. [*Received, January* 13*th,* 1925.]

Crystalline Cuprous Bromide. By DENNIS BROOK BRIGGS.

IN view of the fact that phosphorous acid acts as a powerful reducing agent towards the aqueous solutions of certain metallic salts, it was thought possible that the reaction mixture remaining after the conversion of ethyl alcohol into ethyl bromide might give interesting results.

After the ethyl bromide had been removed from the mixture of 140 c.c. of ethyl alcohol, 40 c.c. of bromine, and 20 g. of red phosphorus taken to produce it, the product remaining in the distilling flask was filtered and the clear syrupy red liquid obtained was added to an excess of cupric sulphate solution. The mixture turned dark green and on boiling for a few minutes a white, crystalline precipitate began to form. This proved to be cuprous bromide, which remained white until, after repeated washing, it began to assume a yellow tint.

The substance dissolved readily in concentrated hydrochloric acid, and this solution gave the usual reactions of a cuprous salt. Tests for acid radicals (other than a bromide) which might possibly be present, gave negative results. Copper in the cupric state was also absent.

Cuprous Iodide.—The same method of treatment with the product of the reaction between ethyl alcohol, iodine, and red phosphorus (after removal of ethyl iodide) yielded a dark solution which on dilution precipitated iodine. This solution, when boiled with cupric sulphate, gave a precipitate of cuprous iodide.—BRAD-FIELD COLLEGE, BERKS. [*Received, December* 29*th,* 1924.]

The Molecular Weight of Cholesterol. By JAMES RIDDICK
PARTINGTON and SIDNEY KEENLYSIDE TWEEDY.

IN a communication to this Journal (1911, **99,** 313) one of the authors described some experiments on the freezing points of mixtures of cholesterol with palmitic, stearic, and oleic acids, which were intended to show that these substances do not deposit compounds from melts. The results obtained, however, are cap-

able of throwing light on the complexity of the cholesterol molecule.

The curves shown in the paper indicate that the depression on the acid side is practically linear, and in the case of palmitic acid a depression of $0.1°$ per g. of cholesterol in 100 g. of acid is calculated. It has been found (Stratton and Partington, *Phil. Mag.*, 1924, [vi], **48**, 1085) that the molecular depression for very pure palmitic acid (m. p. $62.25°$), with mesitylene as solute, is $43.13°$. A determination of the latent heat of fusion of the acid also showed that, contrary to previously recorded data, the freezing-point lowering is normally related to the latent heat.

If we now calculate the molecular weight of cholesterol from these data, we find $M = 43.13°/0.1° = 431$. The molecular weight calculated from the formula $C_{27}H_{46}O$ is 386. The result confirms the supposition that solid solutions are not deposited on cooling the melt.

Further experiments have been made on the depression of the freezing point of benzene, and the elevation of the boiling points of benzene and alcohol, produced by dissolved cholesterol. The latter was prepared from gall-stones by crystallisation from alcohol, had a m. p. of $148°$, and was just fused before weighing out. The results obtained were as follows.

A Landsberger–Beckmann apparatus was used for the b. p. determination, redistilled Kahlbaum's benzene being used as solvent.

Expt.	G. of cholesterol.	Vol. of solution in c.c.	Elevation of b. p.	M.
1	0.788	15.12	0.32°	424
2	0.4288	14.7	0.225	424
3	0.8488	{ 10.5	0.61	434
		{ 14.28	0.46	423

(The molecular elevation per 100 c.c. is taken as 32.8 for benzene and 15.6 for alcohol.)

A b. p. determination made in pure, redistilled alcohol gave :

4	0.4749	13.65	0.127	427

The freezing-point measurements were made with the usual apparatus. The results were as follows :

Expt.	G. of cholesterol.	G. of benzene.	Obs. depression.	M.
1	0.333	22.709	0.178°	423
2	0.230	18.600	0.157	405
			(2 expts.)	

The molecular depression for benzene is taken as 51.39 per 100 g. (Stratton and Partington, *loc. cit.*).

If the normal molecular weight of cholesterol is 386, the above results indicate some association in solutions in benzene, alcohol, and palmitic acid. The mean of all the results gives a mol. wt. of 423.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON. [*Received, October 21st, 1924.*]

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*2-Nitro-*m-*cresol and 2-Amino-*m-*cresol.* By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

A MODIFICATION of Gibson's method of nitrating *m*-cresol (J., 1923, **123**, 1269), which obviates the troublesome process of purification by acetylation, consists in using stronger oleum (15% SO_3 instead of 6—7%) for the initial disulphonation and completing this by heating on the water-bath at 50° for ½ hour prior to nitration. Only the first third of the steam-distilled 2-nitro-*m*-cresol comes over as an oil (which subsequently solidifies); the bulk of the distillate solidifies immediately (m. p. 39°). An increased yield is thereby obtained, *viz.*, a minimum of 72 g. from 65 c.c. of *m*-cresol.

One of the authors (H. H. H.) has found the method serviceable for the preparation of 3-chloro-2-nitrophenol.

2-Nitro-3-methoxytoluene, prepared by treating 2-nitro-*m*-cresol in caustic alkali solution with methyl sulphate, was obtained as a colourless product, volatile with steam, and slowly crystallised in characteristic, large, hexagonal plates, m. p. 49°, from the distillate. Gibson's fractionation in a vacuum, etc., was thus avoided.

2-Bromo-3-methoxytoluene was obtained from the above after reduction with stannous chloride and application of the Sandmeyer reaction : a yellow oil, volatile with steam and solidifying in hexagonal plates, m. p. 35·5—36·5° (Found : Br = 39·6; calc., 39·8%). It resists oxidation by dilute nitric acid or neutral or alkaline potassium permanganate.

*2-Amino-*m-*cresol.*—2-Nitro-*m*-cresol (16·5 g.) dissolved in 200 c.c. of water containing 30 g. of sodium carbonate, was treated at the b. p. with solid sodium hydrosulphite (63 g.), 2-amino-*m*-cresol being deposited, on cooling, in colourless, elongated, hexagonal plates, m. p. 150°. Yield 11 g. (Found : N = 11·2; calc., 11·4%).

A poor yield of *2-bromo-*m-*cresol*, m. p. 56—57°, was obtained from it by the Sandmeyer method (Found : Br = 42·5; calc., 42·8%).—COLOUR CHEMISTRY DEPARTMENT, TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December 17th, 1924.*]

LXX.—*The Influence of Acid Concentration on the Oxidation-Reduction Potential of Cuprous and Cupric Chlorides.*

By Sydney Raymond Carter and Frederick Measham Lea.

An extended study of the oxidation potential of cuprous-cupric salts has been rendered desirable in view of the oxidising properties of sulphur dioxide towards cuprous chloride in strongly acid solution.

The reducing action of sulphur dioxide on cupric chloride in aqueous solution has long been known. The oxidation of cuprous chloride in strong hydrochloric acid solutions by sulphur dioxide has been investigated by Wardlaw and Pinkard (J., 1922, **121**, 210), who concluded that in hydrochloric acid solutions of $1 \cdot 5N$ and upwards the primary reaction proceeds according to the equation $2Cu_2Cl_2 + SO_2 + 4HCl = 4CuCl_2 + 2H_2O + S$; and this process was considered to be reversible. The formation of sulphides of copper also observed was attributed to secondary reactions.

The percentage oxidation in hydrochloric acid of definite concentration was found to depend on the initial cuprous chloride concentration, the degree of oxidation being progressively greater as this concentration increased. This was explained by these workers on the basis of some results obtained by Poma (*Atti R. Accad. Lincei*, 1909, [v], **18**, i, 192), who found that, for a definite hydrochloric acid concentration, as the concentration of cupric chloride increased, the amount of cuprous chloride which could be dissolved increased enormously, whilst the number of free cuprous ions showed only a very small increase, indicating that the cuprous copper was present in the form of a complex ion. From this they inferred that, if a mixed cuprous-cupric solution be established (the potential of which would be equal to that of the sulphur dioxide at equilibrium), a greater proportion of cupric salt must be produced in the more concentrated than in the more dilute cuprous chloride solution in order that the necessary free cupric ions should be present to give the requisite oxidation potential.

The following conventions are used in this paper. (1) Square brackets denote concentrations; thus [Cu^I] and [Cu^{II}] denote total salt concentrations, and [Cu$^{\cdot}$] and [Cu$^{\cdot\cdot}$] the corresponding ionic concentrations. (2) Potentials of half-electrodes are referred to the absolute scale. The following values for the $E.M.F.$ of the standard half-elements have been assumed: normal calomel electrode, $0 \cdot 560$ volt, and the mercurous sulphate electrode (N-$H_2SO_4 = 49$ g. per litre), $0 \cdot 966$ volt. (3) For convenience, when considering com-

s 2

plete cells made up of an unknown half-element and a standard half-element, a positive sign, given to the $E.M.F.$ of the entire cell, indicates that positive electricity is flowing from the standard half-element to the unknown through the solution.

The potential of the cuprous-cupric chloride cell was investigated by Poma (*loc. cit.*) for solutions in hydrochloric acid up to $4N$ at 25°, and no attempt was made to keep the cuprous and cupric concentrations constant, solutions, saturated with respect to cuprous chloride, being used with varying concentrations of cupric chloride. These data are therefore of little use for the présent purpose, even within the limited acid region over which they extend.

An investigation was therefore carried out in which the acid concentration ranged from N to $11\cdot5N$ and steps were taken to correct for the diffusion potential between the standard electrode and the strong acid in the oxidation cell.

The complete cells to be investigated were of the following types :

(1) Pt | CuCl CuCl$_2$ xN-HCl | N-HCl | N-KCl | HgCl N-KCl | Hg

$\xleftarrow{\quad}$ a_1 $\xrightarrow{\quad}$ π $\xrightarrow{\quad}$ e_1 $\xrightarrow{\quad}$ $0\cdot560$

(2) Pt | CuCl CuCl$_2$ xN-HCl | N-HCl | N-H$_2$SO$_4$ | Hg$_2$SO$_4$ N-H$_2$SO$_4$ | Hg

$\xleftarrow{\quad}$ a_2 $\xrightarrow{\quad}$ π $\xrightarrow{\quad}$ e_2 $\xrightarrow{\quad}$ $0\cdot966$
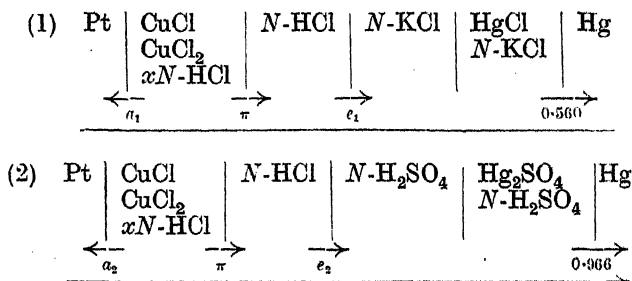
The diffusion boundaries to be considered are π, e_1, and e_2. An alteration of the xN-HCl concentration would cause a variation of the potential π, but the potential e_1 (or e_2) would always be constant. To obtain the true variation of the oxidation potential, a_1 (or a_2), with acid concentration from the measurements of the complete cells 1 and 2, it is only necessary to know the alteration in the potential π corresponding with a change in the value of x; this was determined in a separate investigation (Carter and Lea, preceding paper, p. 487).

EXPERIMENTAL.

The cuprous-cupric solutions were made up with pure crystallised cupric chloride and anhydrous, white cuprous chloride, the latter being specially prepared and kept in sealed tubes until required (compare J., 1922, **121**, 210).

The cells were made up as nearly as possible to the cuprous, cupric and hydrochloric acid concentrations required and, after the

completion of the potential measurements, were analysed as follows. The cupric copper was estimated by direct titration of a known volume with titanous chloride in presence of a known amount of iron, a large excess of potassium thiocyanate being used as indicator (see Knecht and Hibbert, " New Reduction Methods in Volumetric Analysis," p. 55).

The total copper in 10 c.c. was determined by oxidising the cuprous chloride with sodium peroxide, diluting, and boiling the solution for 15 minutes; the solution was cooled, made up to 100 c.c., and an aliquot portion titrated with titanous chloride as before. The cuprous copper was thus obtained by difference. The total chloride was estimated gravimetrically, and the free hydrochloric acid calculated.

Precautions were taken to prevent oxidation of the cuprous chloride by air while the preparation of the cells, the potential measurements, and the subsequent analysis were in progress. The solutions were maintained in an atmosphere of nitrogen throughout these operations. Two or more indifferent electrodes of platinised platinum were used in each cell and identical values were always obtained. All measurements were made at 18°.

Liquid Connexions.—Liquid connexion with the cuprous-cupric element was made by tubes, fitted with taps, filled with the cell electrolyte and dipping into a similar solution. Connexion between this xN-hydrochloric acid and the N-hydrochloric acid was made by inverted U-tubes filled with N-hydrochloric acid. These tubes were about 3 mm. in bore, and the ends were plugged with filter-paper. Liquid connexion between the N-hydrochloric acid and the standard half-element was made in a similar manner, the U-tube in this case, however, being filled with the standard half-element electrolyte.

Influence of Acid Concentration.—A series of cells was examined in which the acid concentration varied from N to $11\cdot5N$. The cuprous and cupric chloride concentrations were as nearly as possible the same and equal to $0\cdot1N$, the total copper concentration thus being $0\cdot2N$. (*Note.*—A " normal solution " signifies one gram-atom, 63·57 grams of copper per litre.) The results were subsequently corrected to the ratio $[Cu^{I}]/[Cu^{II}] = 1\cdot000$ by means of the logarithmic formula

$$E = E_0 - RT/nF. \log [Cu^{I}]/[Cu^{II}].$$

The correction to be applied was never greater than $0\cdot001$ volt in this series, and its average value was about $0\cdot0005$ volt.

Cell 1 was subject to slight fluctuation (up to $0\cdot0015$ volt) on keeping, but cell 2 remained almost constant. This was un-

doubtedly due to fluctuation in the diffusion potential set up at the N-HCl|N-KCl boundary; the N-HCl|N-H$_2$SO$_4$ boundary remained without appreciable alteration. For this reason, the potentials against the mercurous sulphate electrode are probably more trustworthy than those against the calomel electrode.

In this way, the $E.M.F.$'s of the entire cell, which are denoted by x and y in cells 1 and 2, respectively, were obtained and the results are given in Table I. Acid concentrations are recorded in gram-equivalents per litre.

TABLE I.

Series X. [Cu^{I}] = [Cu^{II}] = 0·1N.

[HCl].	E.M.F. (volt).		[HCl].	E.M.F. (volt).	
	x.	y.		x.	y.
11·67	+0·2047	−0·1802	4·63	+0·2276	−0·1579
9·23	0·2160	0·1683	3·99	0·2159	0·1670
7·74	0·2241	0·1601	2·97	0·1977	0·1863
6·77	0·2282	0·1557	2·03	0·1781	0·2073
6·12	0·2307	0·1549	1·39	0·1592	0·2248
5·56	0·2282	0·1563			

It is seen that the cuprous-cupric potential has a maximum value in about 6N-acid.

A further series, Z, consisting of cells in which the cuprous and cupric chloride concentrations were 0·025N, was similarly examined.

TABLE II.

Series Z. [Cu^{I}] = [Cu^{II}] = 0·025N.

[HCl].	E.M.F. (volt).		[HCl].	E.M.F. (volt).	
	x.	y.		x.	y.
11·56	+0·2011	−0·1831	6·37	+0·2302	−0·1556
10·35	0·2081	0·1766	5·89	0·2289	0·1556
9·86	0·2118	0·1712	5·07	0·2251	0·1580
8·01	0·2221	0·1617	3·48	0·2105	0·1742
7·80	0·2251	0·1594	3·39	0·2093	0·1761
7·39	—	0·1584	2·49	0·1866	0·1981
6·50	0·2296	0·1558	1·545	0·1627	0·2229

It is obvious from comparison with Table I that, over the range of acid concentration investigated, the potentials for low copper concentrations are independent of the total copper concentration. Curves of potential against acid concentration are almost identical and superimposable.

Corrections for Diffusion Potential and Calculation of Absolute E.M.F.—Referring to the cells of types 1 and 2, the points of potential difference and their direction of action have been indicated.

The potentials x and y of the complete cells as obtained from Series X, Table I, will be employed. The values of π are taken from the preceding paper. The potentials e_1 and e_2, calculated,

on the basis of Henderson's formula (*Z. physikal. Chem.*, 1907, **59**, 118), from conductivity data are 0·0288 volt and 0·0065 volt, respectively.

Consider cell 1 and let the potential of the half-element $(Pt)|CuCl,CuCl_2,xN$-HCl be a_1. If the total *E.M.F.* of the complete cell be x, then a_1 (volts) $= x + \pi + 0 \cdot 0288 + 0 \cdot 560$. Similarly for cell 2, if a_2 denotes the *E.M.F.* of the half-element $(Pt)|CuCl,CuCl_2,xN$-HCl as obtained from cell 2, then $a_2 = y + \pi + 0 \cdot 0065 + 0 \cdot 966$.

The results are tabulated below, and for convenience the acid concentrations are given in whole numbers, the values of x and y being taken from curves plotted from Series X, Table I.

<div align="center">TABLE III.</div>

<div align="center">*E.M.F.* (volt).</div>

[HCl].	x.	y.	π.	a_1.	a_2.
1·0	+0·149	−0·236	0·0000	0·7378	0·7365
2·0	0·1766	0·2075	0·0163	0·7814	0·7813
3·0	0·1988	0·1850	0·0296	0·8172	0·8171
4·0	0·2159	0·1675	0·0400	0·8447	0·8450
5·0	0·2256	0·1576	0·0505	0·8649	0·8654
6·0	0·2301	0·1545	0·0591	0·8780	0·8771
7·0	0·2272	0·1565	0·0674	0·8834	0·8834
8·0	0·2227	0·1618	0·0726	0·8841	0·8833
9·0	0·2176	0·1669	0·0770	0·8834	0·8826
10·0	0·2126	0·1720	0·0806	0·8820	0·8811
11·0	0·2075	0·1772	0·0839	0·8802	0·8792
11·5	0·2050	0·1798	0·0853	0·8791	0·8780

The agreement between the values of a_1 and a_2 for the cuprous-cupric potential as calculated from measurements against calomel and mercurous sulphate half-element readings, respectively, is satisfactory. The maximum value of a_1—a_2 is of the same order as might be introduced by variation of the diffusion potential e_1.

The values of a_2 are shown plotted against acid concentration in curve 1 (Fig. 1). It is seen that for acid above $6N$ there is very little change in the cuprous-cupric potential.

Discussion of the Causes of the Changes in Oxidation Potential due to Acid Concentration.—The general form of the curve of the cupric-cuprous potential (curve 4, Fig. 1) is very different from that of the ferric-ferrous chlorides (J., 1924, **125**, 1883). In the former case, however, one of the components, cuprous chloride, is almost insoluble in water, but soluble in hydrochloric acid. Moreover, the solubility increases with rise in acid concentration (Engel, *Ann. Chim. Phys.*, 1889, **17**, 376). The cuprous chloride in the solution must therefore be in the form of complex salts or ions, formed by combination with the hydrochloric acid, and consequently the concentration of cuprous ion will be exceedingly small.

(a) The cupric-cuprous potential curve shows a maximum at $7N$—$8N$, which is approximately the same acid concentration as the maximum in the ionic concentration curve for hydrochloric acid in Table IV as calculated from Green's formula,

$$[Cl'] = a\,[HCl] = (\Lambda_v/\Lambda_\infty)\,(\eta_v/\eta_0)^{0\cdot55}\,[HCl]$$

(J., 1908, **93**, 2023.   The conductivity data are taken from Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1898, pp.

FIG. 1.

Oxidation potentials of cupric and cuprous chlorides in hydrochloric acid.
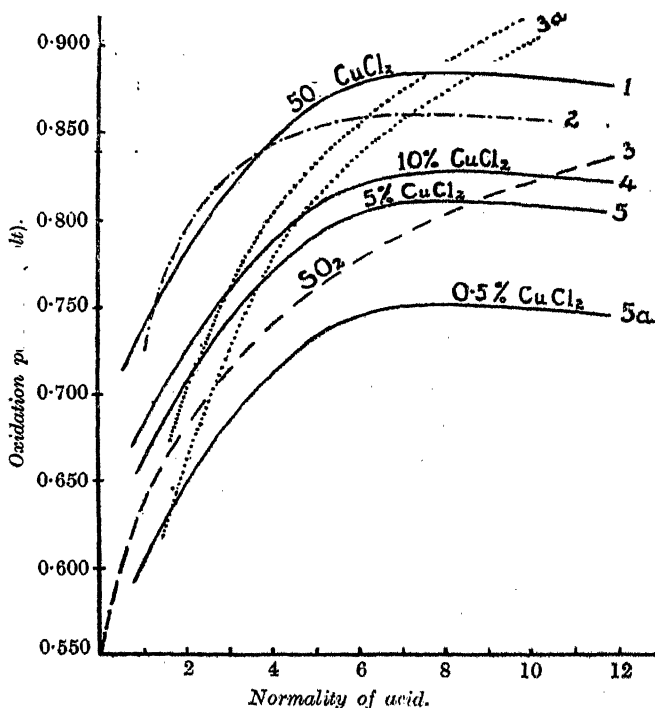
154, 160, and the viscosity data from Landolt-Börnstein " Tabellen," 1912, p. 83, and Taylor and Ranken, *Proc. Roy. Soc. Edin.*, 1904, **25**, 231—241).

TABLE IV.

[HCl] ...	1·00	2·00	3·00	4·00	5·00	6·00	7·00	8·00	9·00	10·00
[H˙] or [Cl']	0·82	1·42	1·83	2·12	2·30	2·38	2·39	2·37	2·35	2·32

This may be explained by the fact that cuprous chloride and hydrogen chloride are known to form compounds $H_2Cu_2Cl_4$ and H_2CuCl_3, which would give rise to the ions Cu_2Cl_4'' and $CuCl_3''$,

the formation of the latter being the more likely in strong hydro-chloric acid solution (Bodländer and Storbeck, *Z. anorg. Chem.*, 1902, **31**, 1; Noyes and Chow, *J. Amer. Chem. Soc.*, 1918, **40**, 739).

Assuming the existence of the compound H_2CuCl_3 in solution, it may be shown that $[Cu^{\cdot}] = k[Cl']^5$ and hence $E = E_0 + 0.058$ log $[Cl']^5$, where E_0 is the value when $[Cl'] = 1.00$.

The values of E which have been calculated from this equation by means of the data for $[Cl']$ recorded in Table IV are plotted in curve 2 (Fig. 1) for comparison with the cupric-cuprous potential (curve 1) based on values given in Table III.

The two curves show a close resemblance, but the agreement may to a certain extent be accidental, since there are two weak points involved in the above deductions. It is questionable whether the $[Cl']$ could be deduced accurately from conductivity-viscosity data for concentrated hydrochloric acid solutions. Moreover it is doubtful whether the law of mass action would apply in such an instance.

(*b*) It is also possible that considerable complex formation may take place in solution between cupric chloride and hydrogen chloride, since, at 0°, Foote identified a solid compound, $CuCl_2,HCl,3H_2O$, in acid of concentration above 31% (*J. Amer. Chem. Soc.*, 1923, **45**, 663). In this case, free cupric chloride would be removed thus :

$$CuCl_2 + nHCl = CuCl_2,nHCl.$$
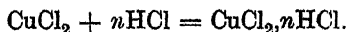
Consequently, with increasing $[HCl]$, the $[Cu^{\cdot\cdot}]$ would be diminished according to the equation

$$CuCl_2 = Cu^{\cdot\cdot} + 2Cl'.$$

This would result in a steady diminution in *E.M.F.* with rise in $[HCl]$ such as is observed in the ferric-ferrous potentials, and would produce an effect opposed to that described in the previous paragraph (*a*).

Probably both factors are operating. At low acid concentrations, the changes in cuprous ion outlined in (*a*) are producing the rise in potential, whilst at high acid concentrations the changes in cupric ion indicated in (*b*) come into play, a maximum being pro-duced in about 7*N*- to 8*N*-hydrochloric acid.

Complex Formation between Cuprous, Cupric, and Hydrogen Chlorides.—On adding a green solution of cupric chloride in hydro-chloric acid to a colourless solution of cuprous chloride, also in hydrochloric acid (or even to white, solid cuprous chloride), a dark brown compound was at once formed and for high copper concen-trations the solution so obtained was extremely dark in colour. The formation of this complex also appears to be dependent on the chlorine-ion concentration, since, for a given series, such as X,

s*

the colour of the solution (in which $[Cu^I] = [Cu^{II}] = 0.1N$) changed from light green to yellow-brown on increasing the acid concentration.

The production of this brown compound was also observed by Poma (*loc. cit.*), who states that, on electrolysis, it migrates to the anode and hence must be negatively charged. The constitution of this complex is unknown, but its formation will obviously lead to deviations from the above fifth-power relation.

The Applicability of the Logarithmic Law.—In view of the large degree of complex formation that occurs in solutions of the copper chlorides in hydrochloric acid it was doubtful whether the logarithmic law for changes in the cuprous-cupric ratio would hold, and therefore a series of cells was made at constant acid concentration with varying proportions of cuprous and cupric chlorides. In the following series (A), the total copper concentration was approximately equal to $0.2N$, whilst the acid concentration in all cases was $9.0N$. Row 2 shows the observed *E.M.F.* of the cell complete with a standard calomel half-element. Row 3 shows the value of the normal potential, E_0, as obtained from the data in row 2 by the formula $E_0 = E + RT/F . \log [Cu^I]/[Cu^{II}]$ after correcting for all diffusion potentials and allowing for the calomel electrode.

TABLE V.

Series A. $[HCl] = 9.0N$.

1	$[Cu^I]/[Cu^{II}]$		0.1314	0.348	1.000	6.93	21.95	27.65
2	E (calomel). Volt.		0.2628	0.2441	0.2179	0.1680	0.1432	0.1380
	. Volt.		0.8775	0.8833	0.8837	0.8825	0.8869	0.8875

From the values of E_0 it is seen that the logarithmic law holds fairly closely, but that the deviations from it become appreciable when extreme ratios are considered. In order to test this for other acid concentrations, further measurements in $6.17N$-hydrochloric acid were carried out. Two cells were measured, with $[Cu^I]/[Cu^{II}]$ equal to 1.00 and 0.3143, respectively. The observed change in potential was 0.0273 volt, while that demanded by direct application of the logarithmic law is 0.029 volt. The deviation is again small, and hence over moderate ratio changes the logarithmic law may be applied with little error.

Effect of Total Copper Concentration.—A further series (C) of cells was investigated, high concentrations of the copper chlorides being used, to test the general effect of high total copper concentration on the potential. Considerable difficulty was encountered in making the potential measurements. Fluctuations of the *E.M.F.* up to 0.005 volt took place, according to the degree of mixing which occurred at the aN-CuCl,bN-CuCl$_2$,xN-HCl$|N$-HCl liquid boundary. This was ascribed to the influence of the high copper

concentrations, since, under these conditions, the current across the boundary would not be carried in its entirety by the hydrogen and chlorine ions, as would be the case with the very low copper concentrations previously employed. It is a similar effect in a more marked degree to that already found obtaining in the case of the KCl|HCl boundary. In all cases, the initial potential values measured after making first contact and obtaining a sharp boundary were used, as these were the most consistent and reproducible of all the results obtained.

The results obtained in this series (C) are given in Table VI. The total copper concentrations were high in all cases, but were not kept constant as hitherto. The acid concentration was $8.45N$. Column 4 shows the $E.M.F.$ of the cell complete with a calomel half-element. Column 5 shows the value of E_0 obtained from data recorded in column 4, after correction for all diffusion potentials as before.

<div align="center">

TABLE VI.

Series C.   [HCl] = $8.45N$.

</div>

$[Cu^I]$.	$[Cu^{II}]$.	$[Cu^I]/[Cu^{II}]$.	ϵ (volt).	E_0 (volt).
0·099	1·112	0·089	0·2874	0·8896
0·698	1·175	0·594	0·2413	0·8915
0·905	0·958	0·945	0·2326	0·8945
1·925	0·350	5·50	0·1896	0·8959
2·78 *	0·122	22·84	0·1611	0·9031

<div align="center">

* This cell contained a saturated solution of cuprous chloride.

</div>

The values of E_0 given in column 5 show that, even for concentrated solutions, the deviations from the logarithmic law are comparatively small, though they become appreciable when extreme ratios are considered and when the cuprous chloride concentration begins to approach the saturation point.

The general conclusion may be drawn, from Series A and C, that the logarithmic law is roughly applicable for changes in the cuprous-cupric ratio, for any concentration of total copper and acid, over moderate ranges, but does not hold when very large ratios are considered.

Action of Sulphur Dioxide on Cuprous and Cupric Salts.

(a) *Influence of Acid Concentration.*—The cuprous-cupric potentials when $[Cu^I] = [Cu^{II}] = 0.1N$, as given in Table III, are plotted in curve 1, Fig. 1.

The potentials for mixtures containing 10·0, 5·0, and 0·5% of cupric-copper have been deduced by the logarithmic formula $E = E_0 + 0.058 \log [Cu^{II}]/[Cu^I]$ and are shown in curves 4, 5, and 5a, respectively.

The limiting ratio for which the logarithmic formula holds is

practically 5% and the potential for the 0·5% mixture is therefore somewhat higher. The sulphur dioxide oxidation potential as obtained by Carter and James (J., 1924, **125**, 2231) is plotted against acid concentration in curve 3. Too much reliance, however, should not be placed on this curve, as the potentials refer to a process which is probably not strictly reversible. The band 3a indicates the region in which sulphur dioxide is neither reduced nor oxidised, as inferred from the ferrous-ferric salts (Carter and Clews, J., 1924, **125**, 1887). The $E.M.F.$'s on this diagram are on the absolute scale and have been corrected for diffusion potentials. The values are therefore somewhat higher than in the corresponding figure for the ferrous–ferric salts, in which the diffusion potential has not been eliminated. Any cuprous-cupric mixture in a mixture of definite concentration will establish a certain oxidation-reduction potential, and the magnitude of this potential compared with that required for the reduction of sulphur dioxide will determine the amount of reaction which takes place and its direction. When these two potentials are equal, a condition of equilibrium will exist; and, in general, reaction will occur until this state is established.

An inspection of the curves indicates that cupric chloride should be reduced to a certain extent by sulphur dioxide in concentrated acid solution, although the reaction would not proceed to completion. This is in accordance with the experiments of Wardlaw and Pinkard (J., 1922, **121**, p. 217, Tables V and VI). In faintly acid solution also, reduction should occur, but even here the reaction would probably be incomplete; for example, when cuprous chloride prepared by the reduction of cupric chloride with sulphur dioxide is being washed with dilute sulphur dioxide solution the liquor invariably has a blue tinge. Nevertheless a colourless specimen of the cuprous chloride can be obtained if the cupric salt is removed by rapid filtration. A considerable portion of the sulphur dioxide curve lies above the cuprous curve (cupric/cuprous = 0·5/99·5) and in such cases sulphur dioxide acts as an oxidising agent towards cuprous salts. Between N- and $4N$-acid the difference is slight and the percentage oxidation to be expected is small. Over part of this range cuprous sulphide also is formed, but the main factor regulating the reaction is evidently the difference in potential between the cuprous-cupric chloride and the sulphur dioxide (Wardlaw and Pinkard, *loc. cit.*, p. 215, Table III, exp. 13—18; p. 216, Table IV).

At an acid concentration of $6N$ the cuprous and sulphur dioxide potential curves diverge considerably, hence for $6N$-acid and upwards the tendency for cuprous chloride to be oxidised by sulphur dioxide increases (*loc. cit.*, p. 215, Table III, exp. 10 and 11).

Since 6 is approximately the normality of the constant-boiling mixture of hydrogen chloride and water, this is the prevailing mixture; in the earlier stages, however, before the excess of hydrogen chloride has been driven off, the acid would be stronger than this for a time.

(b) *Influence of Copper Concentration.*—Reference has already been made to the effect of initial cuprous chloride concentration on the degree of oxidation obtained and also to the theory advanced to explain it.

FIG. 2.

Influence of total copper concentration on oxidation potential.

Log [Cu^I]/[Cu^{II}].
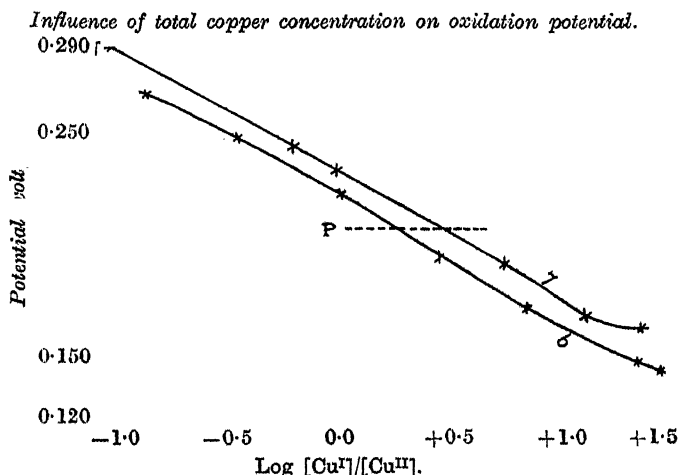
Curves 6 and 7 (Fig. 2) have been plotted from the A and C series of experiments given in Table V, row 2 and Table VI, column 4, respectively, in which the acid concentration was maintained constant while the cuprous-cupric ratio was varied. Both curves have been corrected to the same acid concentration ($8.45N$), and hence curve 7 gives the potential for any given cuprous-cupric ratio, when the total copper concentration is large ($>1.5N$), whilst curve 6 gives the corresponding potential when the total copper concentration is low ($0.2N$). Curve 7 shows a uniformly higher potential than curve 6 for any given cuprous-cupric ratio. Therefore to obtain any given potential P (see curves), a higher proportion of cupric copper is necessary in the case of the low total copper concentration than in the case of the high total copper concentration. This result is not in agreement with the theory advanced by Wardlaw and Pinkard (*loc. cit.*) to account for the fact that the percentage oxidation is progressively higher as the initial concentration of cuprous chloride increases, the actual effect of the total copper concentration on the cuprous-cupric potential

being the reverse of that which they postulated. The potential differences involved between corresponding points on curves 6 and 7 are, however, comparatively small. It is obvious that some other reason must be sought to account for their results and also to explain why the effect observed by these workers is contrary to that demanded by the oxidation-reduction potentials concerned. It will be noted that in the oxidation experiments sulphur dioxide was allowed to pass for 4 hours only and the oxidation values obtained were not expected to be true equilibrium values. In these circumstances, the velocity of the reaction would be one of the main factors determining the degree of oxidation obtained. It is curious, however, that in the analogous case of the chlorides of iron the initial ferrous chloride concentration has a much smaller effect on the degree of oxidation obtained.

Summary.

The cuprous-cupric potential and the various factors affecting it have been investigated.

The true variation in the potential with alteration of acid concentration has been obtained after correction for all diffusion potentials involved.

A theoretical explanation of these changes has been given.

The effect of the cuprous-cupric ratio on the potential has been studied and the logarithmic law shown to hold as a fair approximation over moderate ranges of change in this ratio.

The results have been used to explain the oxidation of cuprous chloride by sulphur dioxide.

LXXI.—*The Action of Light on Chlorine Dioxide.*

By HENRY BOOTH and EDMUND JOHN BOWEN.

WHEN gaseous chlorine dioxide is exposed to light, a large quantity of a red liquid forms on the walls of the vessel (Bowen, J., 1923, **123**, 2328). The photochemical decomposition, therefore, is not that usually represented in text-books :

$$2ClO_2 \rightarrow Cl_2 + 2O_2.$$
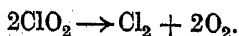
The present paper is an account of experiments to determine the nature of the substances produced. Most of the work was done with chlorine dioxide–carbon dioxide mixtures prepared by Bray's method (*Z. physikal. Chem.*, 1906, 54, 463) on account of the ease of manipulation, and of the freedom from chlorine of the product, but it was proved that similar results were obtained with chlorine dioxide prepared by the much more dangerous potassium chlorate-sulphuric acid process. The gases were dried with phosphorus pentoxide and passed into evacuated glass vessels fitted with taps, which were lubricated sometimes with vaselin and sometimes with phosphoric acid.

On continued exposure to light, the red liquid first obtained from chlorine dioxide becomes colourless. The reaction occurs in the absence of moisture. It was found possible to seal the gas in small glass bulbs, if it were displaced from the capillary leading-in tubes before sealing. Such bulbs containing phosphorus pentoxide as drying agent were kept for 8 weeks in the dark; on exposure, the liquid was produced as in experiments in which the drying had not been so thorough. The pressure in the vessel diminishes during the change.

The liquid boils at about 80° at the ordinary pressure. It dissolves in water with evolution of heat and white fumes, giving a strongly acid solution, from which potassium acetate and alcohol precipitate potassium perchlorate, identified by its optical properties under the microscope. These experiments show clearly that chlorine heptoxide is produced in quantity from illuminated chlorine dioxide. When traces of moisture are present, light, feathery crystals are produced which appear to be the monohydrate of perchloric acid, $HClO_4,H_2O$, m. p. 50°.

An approximate value for the percentage of chlorine dioxide changing to chlorine heptoxide was obtained by exposing the gas to sunlight until the colourless liquid was produced (4—7 hours' exposure). The pressure change was measured, using a narrow-bore mercury manometer with air buffer, which was only connected to the vessel through a tap for brief intervals, and the contents of the flask were washed out and titrated. No chlorine ion was found in the solution. The acidity was assumed to be due to chlorine heptoxide, and the iodine liberated on addition of potassium iodide was assumed to be due to chlorine. An average of numerous experiments showed that chlorine heptoxide formation was 65% by the titration, and 60% by the pressure measurement, of that required by the equation :

$$8ClO_2 \rightarrow 2Cl_2O_7 + 2Cl_2 + O_2.$$
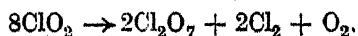
The large formation of chlorine heptoxide is surprising in view of the difficulty of formulating a mechanism of the process. It is inconceivable on collisional probability grounds that the photochemical change is of a high reaction order, and the mechanism must therefore involve a series of consecutive reactions. A simple series cannot be found involving only the known oxides of chlorine. It was shown by comparison of two tubes exposed together, containing chlorine dioxide diluted with oxygen and with an equal volume of carbon dioxide, respectively, that the liquid formation occurred at the same rate in both. Molecular oxygen, therefore, does not appear to play a part in the sequence of changes. It will be seen later that possibly chlorine monoxide is produced, but this is not sufficient to account for the reaction. It is interesting in view of this that Hinshelwood and Prichard (J., 1923, **123**, 2730) found that the thermal decomposition of chlorine monoxide is a consecutive change involving unknown oxides of chlorine, and that Käbitz (*Diss.*, Bonn, 1905) found the same lines in the absorption spectra of chlorine monoxide and chlorine dioxide. It seems clear, then, that in the action of light and heat on chlorine monoxide and chlorine dioxide at least one unknown oxide of chlorine is produced which is very reactive.

In this connexion, the dark red substance colouring the liquid chlorine heptoxide in the initial stages of the photochemical decomposition of chlorine dioxide is of great importance. Unfortunately it was not found possible to obtain results of value by analysing it because of the presence of undecomposed chlorine dioxide and chlorine. Vorländer and Kaascht (*Ber.*, 1923, **56**, [*B*], 1162) found that chlorine dioxide dissolved in anhydrous perchloric acid gave a brownish-red substance. Our substance does not appear to be this, as we found that chlorine dioxide dissolved in a carbon tetrachloride solution of chlorine heptoxide, prepared by Meyer and Kessler's method (*Ber.*, 1921, **54**, 566), gave the characteristic bands of chlorine dioxide only, and did not show the continuous absorption in the blue and violet regions characteristic of the solutions obtained by dissolving the liquid, obtained photochemically, in carbon tetrachloride. On the other hand, the latter resembled the absorption band of chlorine monoxide solutions, and the likelihood that the red substance is chlorine monoxide is increased by the experiments on the thermal decomposition of chlorine dioxide. Dry gaseous chlorine dioxide, prepared in absolute darkness, and diluted with an equal volume of carbon dioxide, was found to remain without decomposition over periods of several hours at temperatures above 85°. When, however, the gas was exposed for a few seconds to an electric lamp, a great difference in the thermal stability was

observed. At 41°, decomposition, as observed with a manometer, took several hours; at 51·5°, it became explosive with a period of induction. At intermediate temperatures, autocatalytic curves with periods of induction were obtained, the reaction rate showing a remarkable sensitivity to temperature. These curious results were always obtained in many concordant repetitions, using different vessels. Additions of small quantities of chlorine or of oxygen were without effect, but moisture retarded the reaction.

Experiment then showed that a little chlorine monoxide added to unilluminated chlorine dioxide exactly reproduced the thermal decomposition curves obtained with the illuminated gas. Analysis of the residual gas showed that chlorine monoxide was still present. It thus seems not unlikely that chlorine monoxide is produced when light acts upon chlorine dioxide, but the explanation of this, and of the formation of the heptoxide, cannot be given by any simple hypothesis.

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LXXII.—*The Nature of the Alternating Effect in Carbon Chains. Part I. The Directive Influence of the Nitroso-group in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD.

THE hypothesis, first advanced by Flürscheim,* that the introduction of a substituent may give rise to an effect which alternates through a whole chain of atoms has met with such success in the interpretation of organic chemical data † that at the present time no one doubts the existence in carbon chains of some property capable of alternating from atom to atom.

The theory has, however, been advanced in two distinct forms. According to Flürscheim's original hypothesis, it is the strength of chemical affinity which alternates. According to the hypothesis of alternating polarities, it is the electric charges (real or latent) on the atoms (Fry, Lapworth, Robinson and others). It happens that both these special interpretations frequently lead to identical pre-

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* It is very difficult to trace the real beginnings of such ideas. Lapworth's αγ-rule may be regarded as a special case of the general proposition, and should be mentioned on account of its early date (1898).

† For applications to aromatic substitution, compare, for example, Flürscheim, *J. pr. Chem.*, 1902, [ii], **66**, 321; 1905, **71**, 497; 1907, **76**, 185; Fry, "The Electronic Conception of Valence," 1921; and for applications to strengths of acids and bases, Flürscheim, *J.*, 1909, **95**, 718; 1910, **97**, 84.

dictions, so that any new experimental illustration (and many have recently been given) of the existence of an alternating effect is not necessarily evidence in favour of either hypothesis. Crucial, and also simple, cases, in which the two hypotheses inevitably lead to opposite predictions, are not easily devised; but it is only by experiments on cases of this kind that an insight into the nature of the alternating effect can be gained.*

The conditions to be fulfilled in such an experiment may be seen from the postulates of the two theories. According to Flürscheim's hypothesis, the substituent atom giving rise to alternation—the " key-atom," to employ Lapworth's convenient name—acts by virtue of its disposable affinity. Tervalent nitrogen and bivalent oxygen both possess more unbound affinity than hydrogen, and, for instance, if attached to the benzene nucleus, will cause the development of free affinity in the *o*- and *p*-positions; that is, they will be *op*-directing. Their relative influence when competing will accord with their relative tendencies to attain a higher valency : tervalent nitrogen will have the greater influence. According to the polar view, on the other hand, it is the negative character of oxygen and nitrogen atoms which renders them *op*-directing, since a group directly entering in place of hydrogen must be positive. When competing, however, oxygen must predominate over nitrogen on account of the greater negativity of the former (*i.e.*, its more complete series of unrestrained electrons; Robinson, *Trans. Faraday Soc.*, 1923, **19**, 506; Kermack and Robinson, J., 1922, **121**, 427 ; Flürscheim, *Chem. and Ind.*, 1924, **43**, 1161). Again, on Flürscheim's hypothesis, effects of the opposite kind must be produced by a substituent atom having less disposable affinity than hydrogen, as, for instance, quinquevalent nitrogen; and the same prediction is achieved for the hypothesis of alternate polarities by treating as the key-atom, not the nitrogen atom itself, but *the more strongly negative oxygen atom* with which the quinquevalent nitrogen atom is usually combined. Thus it follows that the predictions of the two hypotheses are bound to agree as regards the directive effects of almost all the simpler groups.† In order to obtain the evidence sought, it is necessary to set counter to one another the postulated predominating effects of highly unsaturated tervalent nitrogen on

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* The two hypotheses are not of necessity mutually exclusive. Thus Lapworth (*Chem. and Ind.*, 1924, **43**, 766) has admitted the necessity for Flürscheim's interpretation whilst claiming for the theory of alternate polarities an equal position as an additional factor. This possible superposition of alternating effects adds greatly to the difficulty of distinguishing between the two theories.

† Complex groups, especially those bound to the ring through carbon, require special consideration which it is proposed to defer to a later paper.

the one hand and highly electronegative oxygen on the other. The only simple groups fulfilling this condition are the nitroso- and hydroxylamino-groups, and of these the former alone is free from the complicating presence of hydrogen and other possible " key-atoms." The determination of the directive influence of the nitroso-group therefore possesses much greater importance than would normally attach to a similar case, because it is the simplest, indeed, perhaps, the only really simple, case which is crucial for either theory :—
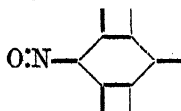
(N = key atom; ∴ free affinity in op-positions; ∴ NO-group is op-directive.)
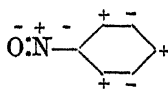
(O = key-atom; * ∴ m-carbon atoms negative; ∴ NO-group is m-directive.)

The facts, so far as they have been ascertained, are that nitroso-benzene can be directly chlorinated, brominated, and nitrated; and that in each case the group introduced enters mainly at the para-position; meta-isomerides could not be detected.†

Summary and Conclusions.—Whilst no inference of a general character can be drawn from these experiments, the results distinctly favour the view that directive effects in aromatic substitution are dependent on an alternation of quantity, rather than of electro-polar quality, of chemical affinity.

EXPERIMENTAL.

(i) *Action of Bromine on Nitrosobenzene.*—A solution of pure nitrosobenzene (5 g.; freshly distilled in steam, crystallised, and dried) in dry carbon disulphide (50 c.c.) was treated as quickly as possible at −5° with a solution of bromine (7·5 g.) in the same solvent (75 c.c.). Most of the solvent and the dissolved hydrogen

* This allocation of signs can also be supported on experimental grounds, since the reactions of the nitroso-group closely resemble those of the carbonyl group, which is always written $-\overset{+}{C} = \overset{-}{O}$. The additions of Grignard reagents, and the condensations with malonic ester, and with amines, hydrazines, etc., may be cited as examples :—

$$C_6H_5 \cdot \overset{+}{N} \overset{-}{=} \overset{-}{O} + \overset{-}{R} \cdot \overset{+}{Mg}Br \longrightarrow C_6H_5 \cdot NR \cdot OMgBr.$$

$$C_6H_5 \cdot \overset{+}{N} \overset{-}{=} \overset{-}{O} + \overset{+}{H_2}\overset{-}{C}(CO_2Et)_2 \longrightarrow C_6H_5 \cdot N : C(CO_2Et)_2 + H_2O.$$
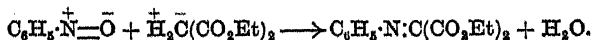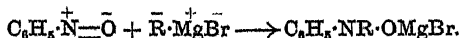
† These results are in agreement with, but simpler than, the indications that have previously been obtained; compare Bamberger, Büsdorf, and Sand (*Ber.*, 1898, **31**, 1513) on the polymerisation of nitrosobenzene, and Ingold and Weaver (*J.*, 1924, **125**, 1456) on its ring additions with other unsaturated substances.

bromide were rapidly removed under diminished pressure, the concentrated solution was diluted with fresh ice-cold carbon disulphide, again reduced to a small volume, and the process repeated a third time. The liquid was then decanted from a small tarry deposit, allowed to evaporate in a current of air, and the crystalline residue distilled in steam, when the nitroso-compounds passed over (blue condensate) during the first 5—10 minutes.

p-*Bromonitrosobenzene.*—From the " nitroso-fraction," pure *p*-bromonitrosobenzene was readily separated by crystallisation from ethyl alcohol. It was identified by its m. p. (95°), by a mixed m. p.* with a specimen prepared by oxidation of *p*-bromoaniline, and by analysis (Found : C = 38·9; H = 2·2; N = 7·6; Br = 42·9. Calc., C = 38·7; H = 2·1; N = 7·5; Br = 43·0%). To make quite certain of its identity, it was condensed with a molecular proportion of aniline (warming for a few minutes in glacial acetic acid solution suffices), and the *p*-bromoazobenzene produced (m. p. 89°; orange leaflets from dilute acetic acid) identified with a specimen prepared in like manner from *p*-bromoaniline and nitrosobenzene. The yield of bromonitrosobenzene was variable, but amounted in some experiments to 40%. Part of the remaining material was accounted for as *pp'*-dibromoazoxybenzene, the normal auto-decomposition product of *p*-bromonitrosobenzene, part as *p*-bromonitrobenzene, its product of oxidation, and a further portion as unattacked nitrosobenzene. Doubtless, azoxybenzene and nitrobenzene also were present, but they were not isolated.

In order to search for possible isomerides the alcoholic mother-liquors from the *p*-bromonitrosobenzene from several experiments such as the above were combined, and evaporated at the ordinary temperature. The solid residue was warmed with an equal weight of aniline dissolved in excess of glacial acetic acid, and the resulting azo-compounds were isolated by dilution with water. Fractional crystallisation alternately from aqueous acetic acid and from ligroin gave a fairly sharp separation into *p*-bromoazobenzene and azobenzene (proof of the presence of unchanged nitrosobenzene in the " nitroso-fraction "), no third substance appearing to be present.

p-*Bromonitrobenzene.*—During the distillation in steam, a small quantity of solid continued to collect in the distillate for some hours after the whole of the nitroso-compounds had passed over. This

* Mixed m. p.'s are not of much value as evidence of identity amongst nitroso-compounds, since these substances have a marked tendency to form mixed crystals. Thus *p*-chloro- and *p*-bromo-nitrosobenzene melt at 93° and 95° respectively, and mixtures of the two melt between these limits. It was for this reason that the procedure of confirming all apparent identities through the corresponding azo-compounds was uniformly employed in these experiments.

product was collected, and crystallised from alcohol, when p-bromo-nitrobenzene, m. p. 125°, was obtained. It was identified by analysis (Found : C = 35·7 ; H = 2·1 ; Br = 39·5. Calc., C =35·6 ; H = 2·0 ; Br = 39·6%), and by a direct comparison with a genuine specimen.

pp'-*Dibromoazoxybenzene*.—The residue which did not distil in steam was crystallised (yellow plates) from benzene and identified as pp'-dibromoazoxybenzene by its m. p. (170—171°), and by a mixed m. p. and comparison with an authentic specimen.

(ii) *Action of Chlorine on Nitrosobenzene*.—This experiment was carried out like the last, and it proceeded in much the same way, except that a larger quantity of nitrosobenzene remained owing to loss of chlorine.

p-*Chloronitrosobenzene*.—After distillation in steam, this substance was separated from nitrosobenzene, and finally purified, by crystallisation from alcohol. Its identity was proved by its m. p. (92—93°), by analysis (Found : C = 50·9 ; H = 3·0. Calc., C = 50·9 ; H = 2·8%), by comparison with a specimen prepared by the oxidation of p-chloroaniline, and by its conversion, by condensation with aniline, into p-chloroazobenzene, orange-red prisms, m. p. 88°, a specimen of which was synthesised for comparison from p-chloroaniline and nitrosobenzene.

As in the previous experiment, the mother-liquors were searched, but, besides p-chloronitrosobenzene, only unchanged nitrosobenzene could be detected.

p-*Chloronitrobenzene and* pp'-*Dichloroazoxybenzene*.—The former, prisms, m. p. 83° (Found : C = 45·7 ; H = 2·5. Calc., C = 45·7 ; H = 2·5%), and the latter, needles, m. p. 155° (alone or mixed with a genuine specimen) were isolated, purified, and identified exactly like the corresponding bromo-compounds (above).

(iii) *Direct Nitration of Nitrosobenzene*.—This is a difficult operation on account of the tendency of the substance to oxidise to nitrobenzene, which, for example, is almost the sole product of the action of 100% nitric acid at 0°. However, experiments with mixtures of nitric acid and phosphorus pentoxide yielded definite evidence of the occurrence of nitration side by side with much oxidation. The best results were obtained by adding freshly-prepared crystalline nitrogen pentoxide to a solution of nitroso-benzene in carbon tetrachloride, containing some phosphorus pentoxide in suspension, and cooled in an efficient freezing mixture (ammonium nitrate). Even under these conditions a considerable amount of nitrobenzene was produced.

p-*Nitronitrosobenzene*.—The product was distilled in a current of steam, and the distillate collected by fractions during the first

½ hour. The oil extracted from each fraction by means of ether was mixed with ligroin after removing the ether, a process which caused the separation of crystals from certain of the later fractions. After crystallisation from alcohol (yellow needles), the substance was identified as *p*-nitronitrosobenzene by its m. p. (116°), by comparison with a specimen prepared from *p*-nitroaniline, and by conversion, by condensation with aniline, into *p*-nitroazobenzene (red leaflets, m. p. 134—135°), which was similarly identified by comparison with a specimen synthesised for the purpose.

The whole of the nitronitrosobenzene produced was not isolated in the free state, but the presence of a certain quantity remaining dissolved in the nitrobenzene was proved by boiling the mixture with an acetic acid solution of aniline, and removing the nitrobenzene in a current of steam after the addition of dilute sulphuric acid. The azo-compound (which appears to be somewhat volatile in steam, although much less so than nitrobenzene) was purified by crystallisation from acetic acid, and identified by direct comparison and by analysis (Found : C = 63·6; H = 4·2. Calc., C = 63·5; H = 4·0%).

LXXIII.—*The Synthesis of Glycols from Atrolactinic Acid.*

By ROBERT ROGER.

THE Grignard reaction was employed in the course of work on asymmetric synthesis (McKenzie, J., 1904, **85**, 1249; 1906, **89**, 365; McKenzie and Wren, J., 1906, **89**, 688; McKenzie and Müller, J., 1909, **95**, 544), for example, in the asymmetric synthesis of atrolactinic acid :

$$Ph \cdot CO \cdot CO_2H \longrightarrow Ph \cdot CO \cdot CO_2 \cdot C_{10}H_{19} \longrightarrow$$
inactive   active

$$OH \cdot CPhMe \cdot CO_2 \cdot C_{10}H_{19} \longrightarrow OH \cdot CPhMe \cdot CO_2H.$$
active   active
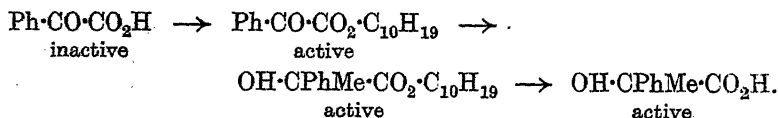
Here the experimental conditions were regulated so that the attack of magnesium methyl iodide on *l*-menthyl benzoylformate took place practically entirely at the carbonyl group to which the phenyl group is attached. A small amount of crude material also was isolated, and this, from its melting point, would seem to have been the pinacol, $OH \cdot CPhMe \cdot CMe_2 \cdot OH$, but this side-issue was not further investigated at the time.

The syntheses of glycols of the type OH·CPhMe·CR$_2$·OH from ethyl atrolactinate by the Grignard reaction has now been investigated and several difficulties were found which were not altogether unexpected. By the action of magnesium methyl iodide on the ester under the usual conditions, only small amounts of the pinacol OH·CPhMe·CMe$_2$·OH were obtained, and with magnesium ethyl iodide the yield of the corresponding glycol was even smaller. By saponification of the resulting oils, a large proportion of the original atrolactinic acid was always recovered, indicating that the ester had been to a large extent unattacked, and that the small yield of glycol could not be attributed to its dehydration (Grignard, *Ann. Chim. Phys.*, 1901, [vii], **24**, 463; Slavjanov, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 140). When magnesium phenyl bromide was employed, however, action seemed to take place to a larger extent, but difficulty was also experienced at first in isolating the glycol from the viscous mass obtained. The use of anisole as the Grignard medium led to no improvement in the yield, just as Meerwein (*Annalen*, 1919, **419**, 121) had found in the action of magnesium ethyl iodide on ethyl diethylglycollate. Finally, I resorted to long periods of heating (11—25 hours) and this led to a marked improvement in the yields.

It would seem, therefore, that the carbethoxy-group in ethyl atrolactinate is very irresponsive to attack by the Grignard reagent, and for this reason the above-mentioned asymmetric syntheses were successful. An interesting light is thrown on the question by Bouvet (*Bull. Soc. chim.*, 1915, [iv], **17**, 202), who subjected ethyl oxalate to the action of various Grignard reagents. With magnesium methyl iodide the yields of pinacol were small, whilst with magnesium ethyl and benzyl halides the actions were restricted almost exclusively to the formation of the respective glycollic esters, OH·CEt$_2$·CO$_2$Et and OH·C(CH$_2$Ph)$_2$·CO$_2$Et. With magnesium phenyl bromide, however, the yield of pinacol from ethyl oxalate was almost theoretical (Valeur, *Bull. Soc. chim.*, 1903, [iii], **29**, 683). Dilthey and Last (*Ber.*, 1904, **37**, 2639) also have investigated the latter reaction, and claim to have isolated β-benzpinacolin, but in proof of their claim they give neither analysis nor any chemical evidence for this compound. The action of magnesium ethyl bromide on ethyl oxalate has been the subject of further investigation by Meerwein (*loc. cit.*), who found that the action can progress a step further with the formation of the hydroxy-ketone, OH·CEt$_2$·COEt, but that this ketone will not react further with magnesium ethyl bromide to give the pinacol. He also obtained the same result starting from ethyl diethylglycollate. The selective action of the Grignard reagent can sometimes be explained by the

practical conditions employed (Hepworth, J., 1919, **115**, 1203),
but the work of Meerwein on ethyl diethylglycollate would show
that in certain examples there is a total inability of the carbethoxy-
group to react completely. The same author also succeeded in
isolating the hydroxy-ketones only in the action of magnesium
propyl and butyl bromides on ethyl diethylglycollate. In contra-
distinction to this, Meerwein (*loc. cit.*) and Parry (J., 1911, **99**,
1169; 1915, **107**, 108) have shown that esters of methylethyl- and
dimethyl-glycollic acids react easily and completely with certain
Grignard reagents.

The formation of pinacols from ethyl oxalate or from disubstituted
glycollic esters is thus often a matter of considerable difficulty.
The selective action of the Grignard reagent in the cases referred
to may be accounted for in two ways. First, the two reactions :
(*a*) ester —→ hydroxy-ester, (*b*) hydroxy-ester —→ pinacol, possess
very different velocities, the second stage being the slower.
Secondly, spatial effects lead to a complex which is not prone to
attack by the reagent. The importance of spatial influences is
well demonstrated in the preparation of *l*-benzoin from *l*-mandel-
amide and magnesium phenyl bromide (McKenzie and Wren, J.,
1908, **93**, 312; 1910, **97**, 473). Here, in spite of the fact that a
moderate excess of reagent was used, the ketol was isolated in
fairly good yield. Moreover, it has since been found in this
laboratory that the addition of a fresh Grignard reagent to the
l-mandelamide-magnesium phenyl bromide complex does not lead
to the formation of a substituted hydrobenzoin unless the *l*-benzoin
is actually isolated.

This reluctance of the carbethoxy-group to react with the Grignard
reagent in the cases mentioned naturally suggests that some form
of steric hindrance had been brought into play. This is supported
by the fact that malonic, succinic, and adipic esters react readily
under similar conditions to those employed for ethyl oxalate, but
good yields of pinacol are obtained (Valeur, *Compt. rend.*, 1901,
132, 834; Bouvet, *loc. cit.*; Zelinsky and Kravetz, *J. Russ. Phys.
Chem. Soc.*, 1906, **38**, 931; Slavjanov, *loc. cit.*). Moreover, when
disubstituted malonic esters are employed, the reaction is restricted
more or less to one carbalkyloxy-group, the controlling factors being,
according to Kalischev (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 427),
both the nature of the substituent and the Grignard reagent groups.

The work carried out by Meerwein and by Tiffeneau on pinacolinic
and semipinacolinic transformations renders those results less ano-
malous. These authors classify the various alkyl and aryl groups
in order of their saturation capacities. Thus, ethyl and benzyl have
a low, methyl and *iso*butyl a moderate, whilst phenyl and other

aromatic groups have a large saturation capacity. That such a conception can play a *rôle* in other directions is demonstrated by, for example, the work of Auwers and Schaich on the alkylation of indazole (*Ber.*, 1921, **54**, 1738) and of Auwers and Wegener on the opening of the ring in substituted coumarones (*J. pr. Chem.*, 1923, [ii], **106**, 226). Similarly, the effect of substitution on the reactivity of the carboxyl group is pronounced when the properties of acetic and triphenylacetic acids are contrasted. Gomberg has shown that the saturating effect of three phenyl groups attached to a single carbon atom is such that tervalent carbon is a practical possibility, and thus in triphenylacetic acid the carboxyl group is rendered very stable. Triphenylacetyl chloride does not therefore react with water readily, owing to the large valency power free to hold the chlorine atom to the carbon :

Compare $\quad \begin{matrix} H \\ H \\ H \end{matrix}\!\!>\!\!C\!-\!C\!\!<\!\!\begin{matrix} O \\ \\ Cl \end{matrix}\quad$ and $\quad \begin{matrix} C_6H_5 \\ C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!\!C\!\cdots\!C\!\!<\!\!\begin{matrix} O \\ \\ Cl \end{matrix}\quad$ [Schmidlin and
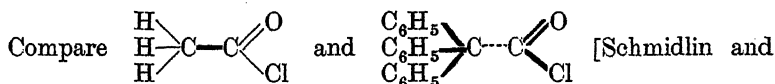
Hodgson (*Ber.*, 1908, **41**, 438)].

Doubtless there will be a variation in the reactivity of the carboxyl groups in the different substituted glycollic acids. Thus, ethyl diethylglycollate will react only partially with a group of small saturation capacity, such as ethyl, giving the hydroxy-ketone. The enfeebling effect of the low capacity of the ethyl group is well marked in Grignard's work on ethyl ethylacetoacetate and ethyl diethylacetoacetate. The former of those compounds, on heating at 100° with magnesium methyl iodide, gave the glycol along with some unchanged ester, but with the latter more than one-half of the ester was recovered unattacked and no trace of the glycol was found. Salkowski (*J. pr. Chem.*, 1923, [ii], **106**, 253) explains this by the formation of an oxonium compound, $O=C<+MgCH_3I \rightarrow$ $>C=O<^{CH_3}_{MgI}$. This reverts readily in the latter case to the original compound, as " sicherlich der Grund liegt in der geringeren Additions-fähigkeit der Carbonyl Gruppe." Ethyl dimethyl-acetoacetate, however, gives fairly good yields of the glycol (Slav-janov, *loc. cit.*). Ethyl methylethylglycollate and methyl hydroxy-trimethylbutyrate react fairly readily with magnesium methyl iodide, but the former reacts better with magnesium phenyl bromide. An ester such as ethyl dimethylglycollate, containing two groups of moderate capacity, reacts with most reagents. Ethyl benzilate reacts very readily with either phenyl or methyl reagents (Acree, *Ber.*, 1904, **37**, 2753; Erdmann, *Inaug. Diss.*, Rostock, 1910).

Ethyl atrolactinate would fall between the two extremes. When

the ester was heated for 3—4 hours with magnesium methyl iodide, a poor yield of pinacol was obtained. The same result was arrived at, starting from ethyl benzoylformate. When magnesium ethyl bromide was employed under similar conditions, the yield was very much smaller, most of the ester being recovered unattacked. On extending the heating period to 20—25 hours, however, a 65% yield of pinacol was obtained. With magnesium phenyl bromide, a good yield of glycol was obtained by heating for 9 hours. The latter glycol was also synthesised by the action of magnesium phenyl bromide on methylbenzoin, OH·CPhMe·COPh, and by the action of magnesium methyl iodide on phenylbenzoin, OH·CPh$_2$·COPh, good yields being obtained in both cases.

EXPERIMENTAL.

β-*Phenyl-γ-methylbutylene* βγ-*Glycol*, OH·CPhMe·CMe$_2$·OH.—The Grignard solution, prepared from methyl iodide (43 g.), was added to an ethereal solution of ethyl atrolactinate (10 g.), the mixture being agitated mechanically. No very vigorous action took place, and the mixture was boiled (4 hours) before decomposition with ice and dilute sulphuric acid. On crystallising the resulting oil from light petroleum, 3·5 g. of solid were obtained (yield 37%). The pure substance, obtained after several crystallisations from light petroleum, crystallised from light petroleum in rosettes of slender needles, m. p. 83·5—84·5° (Found : C = 73·4; H = 8·9. Calc., C = 73·3; H = 9·0%). Lepin (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1165), who prepared the glycol by hydration of the corresponding oxide, gives the m. p. 83—84°. A trace of the glycol gives a faint yellowish-green coloration which assumes a pink tint on standing for some time with concentrated sulphuric acid. The oil obtained from the mother-liquors from the crystallisations gave two products on hydrolysis with caustic potash. (1) By extraction of the alkaline liquors an oil, which did not crystallise, was obtained. (2) By extraction of the acidified liquors, atrolactinic acid (2·1 g.), m. p. 88—90°, was obtained.

The same glycol was also synthesised by the action of magnesium methyl iodide on ethyl benzoylformate as described above. The yield was poor, and was not improved by the use of anisole as the Grignard medium.

ααβ-*Triphenylpropylene* αβ-*Glycol*, OH·CPhMe·CPh$_2$·OH.—Various unsuccessful attempts were made to obtain this glycol from magnesium phenyl bromide and ethyl atrolactinate in the manner described above. It was eventually obtained as follows : Ethyl atrolactinate (20 g.) was added to a solution of magnesium phenyl bromide, prepared from bromobenzene (80 g.), and the mixture was then

boiled for 11 hours. After decomposing with ice and ammonium chloride, an oil was obtained from which 15 g. of crude solid were separated by dissolving in benzene and light petroleum. The pure glycol, m. p. 76—77°, was obtained after several crystallisations from benzene–light petroleum (Found : C = 83·1 ; H = 6·8. Calc., C = 82·9 ; H = 6·6%). With concentrated sulphuric acid, it gives a yellow coloration deepening to an emerald-green.

This pinacol was also synthesised : (1) By the action of magnesium methyl iodide (6 mols.) on phenylbenzoin (1 mol.), prepared from benzil and magnesium phenyl bromide. (2) *Methylbenzoin,* OH·CPhMe·COPh, prepared from magnesium methyl iodide and benzil, crystallises from light petroleum in rosettes of clear needles, m. p. 65—66° (Found : C = 79·3 ; H = 6·35. Calc., C = 79·6 ; H = 6·23%). Methylbenzoin (10 g.; 1 mol.) was added to the ethereal solution of magnesium phenyl bromide (4 mols.). The mixture was boiled for 12 hours, and was then decomposed with ice and ammonium chloride. The pinacol was separated and recrystallised as before (yield 6 g.). Both specimens melted at 76—77°, alone or mixed with the pinacol obtained from ethyl atrolactinate.

β-*Phenyl-γ-ethylamylene* βγ-*Glycol,* OH·CPhMe·CEt₂·OH.—The employment of the same conditions for the preparation of this compound as for the action of magnesium methyl iodide on ethyl atrolactinate gave only meagre yields of the glycol. Another attempt was made by allowing the reaction mixture to remain at the ordinary temperature for 14 days, but the ester seemed to be almost completely unattacked. The use of anisole as the Grignard medium was also unsuccessful. Ultimately, the ester (10 g.; 1 mol.) was heated with magnesium ethyl bromide (12 mols.) for 21 hours, and then decomposed with ice and dilute sulphuric acid. From the ethereal layer, 7 g. of the crude solid were separated. The pure pinacol was obtained by crystallising from light petroleum. Yield 6 g. (Found : C = 75·0 ; H = 9·9. Calc., C = 75·0 ; H = 9·7%).

The glycol crystallises from light petroleum in slender, pointed needles, m. p. 70—71°. It gives a faint yellow-green coloration with concentrated sulphuric acid, and when added to sulphuric acid (d 1·55) it liquefies and develops a marked camphoraceous odour.

LXXIV.—*The Preparation of Pure Methyl Alcohol.*

By HAROLD HARTLEY and HUMPHREY RIVAZ RAIKES.

FOR the purposes of a general investigation of the properties of methyl alcohol as a solvent which is in progress in this laboratory, it was necessary to devise a method by which pure methyl alcohol could be prepared rapidly. The following communication is based on the work of Messrs. A. T. L. Allen, F. K. Ewart, J. E. Frazer, G. Nonhebel, and W. F. K. Wynne-Jones.

In addition to water, the chief impurities which may be present in the commercial alcohol are acetone and formaldehyde : these must be removed before it is dried. Acetone may be estimated either by the sodium hypoiodite method of Bates, Mullaly, and Hartley (J., 1923, **123**, 401), or in the following way, suggested by Mr. J. E. Marsh, F.R.S., which is better adapted to the estimation of very small quantities. Two c.c. of a concentrated stock solution of mercuric cyanide in 6N-sodium hydroxide are added to 2 c.c. of alcohol, and the mixture is warmed to boiling. A white precipitate indicates the presence of a ketone; if the precipitate darkens on standing, the presence of an aldehyde or of a mixture of aldehyde and ketone is inferred. These precipitates settle rapidly, and their bulk may be compared with those produced by alcohol containing known amounts of aldehyde or acetone. When the impurities are present singly, 0·002% of acetone or 0·004% of formaldehyde can be detected, though at the limit it is difficult to differentiate between the two (W. F. K. W.-J.). When the acetone content was greater than 0·02%, it was removed by the method described by Bates (*loc. cit.*).

Removal of Water.—The usual method of drying alcohol by refluxing over freshly burnt lime for several days (Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2834; McKelvy, *Bull. Bur. Standards*, 1913, **9**, 327) proved to be slow and wasteful, since about 20% of the alcohol was retained by the lime after distillation from a water-bath. Metallic calcium also is unsatisfactory, as it introduces volatile impurities, such as ammonia, which are difficult to remove. Sodium is an inefficient drying agent owing to the equilibrium NaO·CH$_3$ + H$_2$O $\rightleftharpoons$ NaOH + CH$_3$·OH, an objection which applies also, though in a lesser degree, to the use of baryta or lime (compare Crismer, *Chem. Zentr.*, 1904, **1**, 1749; W. A. Noyes, *J. Amer. Chem. Soc.*, 1923, **45**, 857).

It was finally decided to use simple fractionation as the principal means of dehydration (S. Young, *Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, 374), followed by distillation from aluminium methoxide

(McKelvy, *loc. cit.*, p. 364). For the fractionation, Hempel * columns with an effective length of 1·3 metres were connected to the distilling flasks by mercury seals, and mercury cups were also provided at the still-heads for the thermometer, contact between hot alcohol vapour and cork being thereby avoided. Soda-lime tubes were attached to the receiver, and all corks were covered with tin-foil. After its boiling point had become constant to 0·05°, the alcohol was fractionated once more and then refluxed under a column with aluminium amalgam (3 g. per litre) until all the aluminium had reacted, when it was distilled as before. The amalgam was made by warming pieces of thin sheet aluminium with a solution of mercuric chloride in dry alcohol. In all cases distillation was carried out at the rate of two drops a second, the first 50 c.c. and the last quarter of the distillate being rejected. Under these conditions, no difficulty arose from the volatility of aluminium methoxide (compare Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1924, **111**, 275). Magnesium (Bjerrum and Zechmeister, *Ber.*, 1923, **56**, [*B*], 894) was found less satisfactory than aluminium.

For electrochemical work it was necessary to free the alcohol from ammonia and similar volatile impurities. This was accomplished by refluxing it for 6 hours with freshly dehydrated copper sulphate (2 g. per litre) under a short column up which a current of pure dry air was passing. It was then distilled rapidly through this column, condensed in block tin, and run through a conductivity cell of the siphon type into a collecting flask of hard glass. The specific conductivity of any portion of the distillate could thus be determined without risk of contamination. By carrying out the distillation at a very rapid rate, and by rejecting the first runnings, alcohol of specific conductivity 0·04 reciprocal megohms was readily obtained: it was preserved in Jena glass flasks having an " outside ground " cap. Sulphanilic acid (Goldschmidt, *Z. physikal. Chem.*, 1912, **81**, 30) was found less efficient than copper sulphate.

Distillation of the dry conductivity alcohol from silver nitrate in order to free it from reducing agents (Pearce and Mortimer, *J. Amer. Chem. Soc.*, 1918, **40**, 509; Partington, *Trans. Faraday Soc.*, 1923, **18**, 414), a procedure which may introduce other impurities, was found to be unnecessary, no aldehyde being detected by the mercuric cyanide test, and solutions of silver nitrate remaining colourless indefinitely. The distillation from aluminium would remove any oxidation products which might have accumulated during earlier fractionations.

* Dufton's copper spiral type is inapplicable owing to the danger of catalytic oxidation.

Detection and Estimation of Water.—The detection and estimation of small traces of water in methyl alcohol are matters of considerable difficulty. Anhydrous copper sulphate is useless for the purpose, as it forms a slightly soluble, bluish-green compound, stated to be $CuSO_4,2MeOH$ (L. de Bruyn, *Rec. trav. chim.*, 1893, **11**, 112).

For the rapid estimation of the water content with an accuracy of 0·02%, the cuprous acetylide test described by Weaver (*J. Amer. Chem. Soc.*, 1914, **36**, 2462) was found convenient. This is based on the reaction of any water with calcium carbide to form acetylene, which remains dissolved in the alcohol and can be detected with an ammoniacal cuprous chloride solution. The latter is conveniently made fresh for each batch of tests by mixing equal volumes of the following solutions (Solution A : 3 g. of cupric chloride, 6 g. of ammonium chloride, and 9 c.c. of 0·88 ammonia in 100 c.c. of water. Solution B : 12 g. of hydroxylamine hydrochloride in 100 c.c. of water).

Quantitative results could be obtained as follows (G. N.). Two small pieces of carbide are covered with 3 c.c. of dry alcohol. After boiling gently for a minute to remove acetylene from the interstices of the carbide, the liquid is filtered. On addition of the cuprous solution, only a trace of colour should be developed; this serves as a blank test. Meanwhile another 2 c.c. of alcohol are added to the prepared carbide, the tube corked and left for one minute, with occasional shaking. The liquid is then filtered into 1 c.c. of the testing solution. The pink colour which develops is compared with standards of methyl-red. The trustworthiness of the test was confirmed by a series of viscosity measurements (J. E. F.), but being of an empirical nature it is necessary to observe the same procedure in every case. Commercial carbide, which is treated with paraffin during manufacture, is not sufficiently active for this test.

Accurate density determinations admit of the estimation of water to at least 0·01%, but are somewhat lengthy for routine work. We have found (F. K. E.) $d_4^{25°} = 0·78641$ as a mean of four concordant determinations, using two pyknometers and different samples of alcohol. This value is slightly lower than that interpolated from data in the literature.

Relative viscosity determinations in an Ostwald viscosimeter allow of the estimation of water with a limit of 0·025%, as the presence of 0·1% of water increases the time of flow by 0·4%, and with a suitable viscosimeter the time of flow can be determined with an accuracy of one part in a thousand. The absolute viscosity

of alcohol which had been subjected to fractionation alone and to treatment with aluminium also was found to be 0·00545 at 25° (F. K. E.), the viscosity of water at that temperature being taken as 0·00895 (Bingham and White, J., 1913, **103**, 959).   Dunstan and Thole (J., 1914, 105, 782) found 0·00546.

The most sensitive test for water is the determination of the electrical conductivity of a dilute solution of hydrogen chloride in the alcohol, provided that the absence of ammonia has been proved by determining the conductivity of the pure solvent.   Goldschmidt (*Z. physikal. Chem.*, 1924, **108**, 121) has shown that $\Lambda^{25°}$ at 0·001N is depressed from 181·8 to 178·3 by the presence of 0·025% of water.   We have found values of 181·5 and 181·0, indicating that the amount of water in the alcohol was less than 0·01%.

In conclusion, we wish to express our thanks to the Chemical Society for grants which defrayed part of the cost of the work.

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LXXV.—*Studies of Equilibrium in Systems of the Type $Al_2(SO_4)_3$–$M''SO_4$–H_2O.   Part I.   Aluminium Sulphate–Copper Sulphate–Water and Aluminium Sulphate–Manganous Sulphate–Water at 30°.*

By ROBERT MARTIN CAVEN and THOMAS CORLETT MITCHELL.

THE present investigation is part of an attempt to discover a connexion between double-salt formation and differences of electropositiveness between the kations of component salts.   At the same time it is hoped to throw light on the question of the existence of " pseudo-alums."

The previous literature on the subject is for the most part descriptive.   Thus, Klauer (*Annalen*, 1835, **14**, 261) described the preparation of ferrous and magnesium pseudo-alums in presence of excess of sulphuric acid.   Rammelsberg (*Pogg. Ann.*, 1838, **43**, 399) dealt with various naturally occurring double salts containing aluminium sulphate.   Kane (*ibid.*, 1838, **44**, 472) mentioned $MnSO_4,Al_2(SO_4)_3,22H_2O$, apjohnite, a naturally occurring salt found and described by Apjohn (*Proc. Roy. Irish Acad.*, 1839, **1**, 51),

and Wirth (Z. angew. Chem., 1913, 26, 81) discussed the system aluminium sulphate–ferrous sulphate–water.

E X P E R I M E N T A L.

The equilibrium mixtures in the case of the copper sulphate system were obtained as follows : Pure recrystallised copper sulphate and aluminium sulphate were placed with water in separate flasks in a thermostat at 40°. A large vessel, fitted with a cork carrying a stirrer and filtering device, was kept in another thermostat at 30° $\pm$ 0·1°, and in this were placed mixtures in different proportions of the two single salt solutions.

The mixtures were stirred for 3 days, and each resulting solution was then decanted through a filter into a weighing-bottle, both kept at the temperature of the bath. The solid phase also was rapidly drained by suction and transferred while moist to a weighing-bottle. The solution and moist solid phase were then weighed, and made into solutions measuring known volumes.

The copper was estimated iodometrically, and the aluminium was calculated after determination of the total sulphate.

The system $MnSO_4$–H_2O shows a transition point at 26°, whereafter the solubility decreases. It was therefore of no advantage to commence with a solution of manganous sulphate above this temperature. In this case solutions of the single salts, saturated at room temperature, were mixed in the reaction vessel and isothermally evaporated by means of a filtered current of air, with constant stirring. When a solid phase separated, the current of air was stopped, and stirring continued for 3 days, whereafter the solution and solid phases were removed for analysis.

Manganese was estimated by precipitating it as hydrated dioxide [using ammonium persulphate in presence of excess of sulphuric acid as recommended by Knorre (Z. angew. Chem., 1901, 14, 1149)], dissolving the precipitate in standard oxalic acid, and titrating the solution with permanganate. Aluminium was again calculated after the determination of total sulphate.

It has been noted (Britton, J., 1922, 121, 982) that aluminium sulphate hydrolyses above 30°. In the experiments carried out, the amount of hydrolysis in the single solutions from which equilibrium systems were obtained was, however, exceedingly small and was neglected.

All the solutions were extremely viscous, especially in the manganous sulphate system, and considerable difficulty was experienced in handling them. Each result, however, was duplicated.

Results.

The quantities in the tables are expressed as g. per 100 g. of solution (for the solutions) or of moist solid (for the rests).
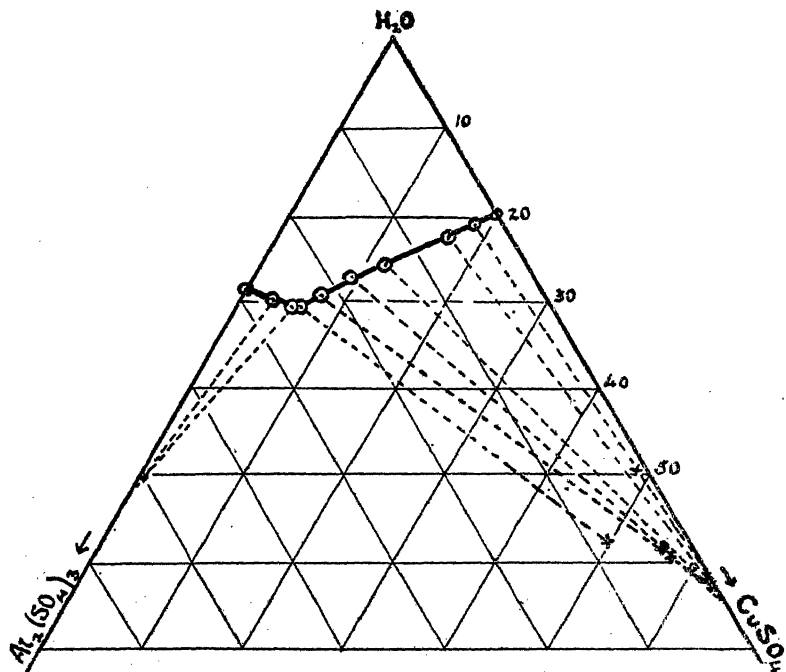
Fig. 1.—*Equilibrium Diagram $Al_2(SO_4)_3-CuSO_4-H_2O$ at 30°.*

That no combination occurs between aluminium sulphate and cupric sulphate is shown by the absence of a double-salt curve, and by the fact that broken lines drawn through "solution" points and appropriate "rests" intersect at points corresponding with the composition of the single salts.

$Al_2(SO_4)_3-CuSO_4-H_2O$ (see Fig. 1).

Solutions.			Rests.		
$Al_2(SO_4)_3$.	$CuSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$CuSO_4$.	H_2O.
nil.	20·33	79·67	—	—	—
2·75	18·65	78·60	0·92	48·61	50·47
5·97	16·76	77·27	0·13	61·72	38·15
13·80	12·13	74·07	1·51	59·38	39·11
17·65	9·79	72·56	3·21	55·25	41·54
22·00	7·67	70·33	2·94	56·69	39·37
24·64	6·30	69·06	8·20	49·78	42·02
25·22	5·74	69·04	50·1	0·30	49·60
26·83	3·39	69·78	49·52	0·25	50·23
28·86	nil.	71·14			
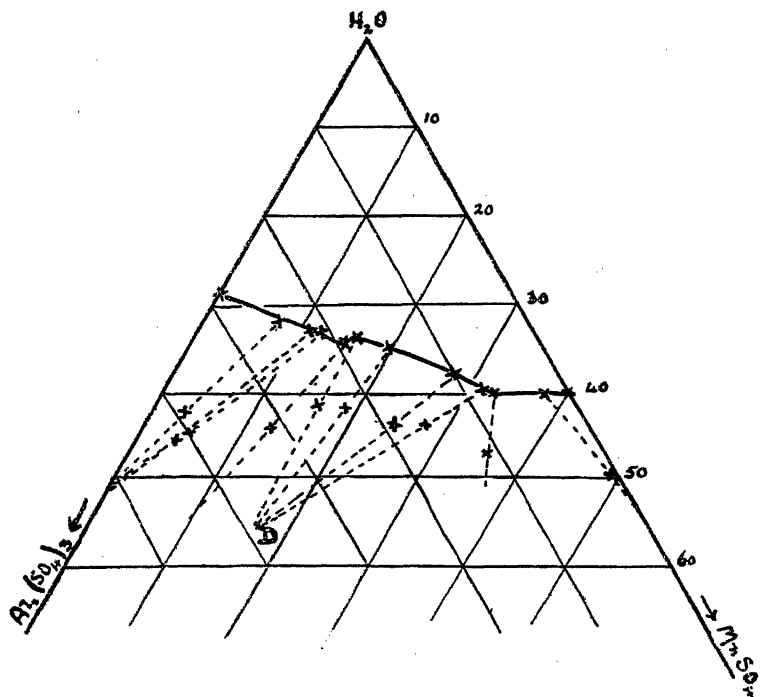
FIG. 2.— *rium Diagram* $Al_2(SO_4)_3$–$MnSO_4$–H_2O *at* 30°.

The existence of a double salt is indicated by the curve intervening between the aluminium sulphate and manganous sulphate curves. The composition of this salt is shown, by the co-ordinates of the point D, at which broken lines drawn through " rests " intersect, to be $Al_2(SO_4)_3,MnSO_4,22H_2O$.

$Al_2(SO_4)_3$–$MnSO_4$–H_2O (see Fig. 2).

Solutions.			Rests.		
$Al_2(SO_4)_3$.	$MnSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$MnSO_4$.	H_2O.
nil	40·03	59·97			—
2·47	37·94	59·59	1·12	49·03	49·85
7·21	32·97	59·82	11·71	35·23	53·06
8·43	31·43	60·14	16·29	27·76	55·95
10·40	27·39	62·21	18·82	24·62	56·56
15·01	19·91	65·08	22·75	19·11	58·14
18·11	15·96	65·93	25·27	16·15	58·58
19·58	15·23	65·19	31·43	12·21	56·36
21·13	12·14	66·73	39·90	4·95	55·15
21·93	11·09	66·98	41·65	4·72	53·63
24·42	7·41	68·17	38·96	3·12	57·92
28·86	nil.	71·14			

Conclusion.—It is evident, in the case of the cupric sulphate system, that no double salt is formed at 30°.

In the manganous sulphate system the compound
$$Al_2(SO_4)_3,MnSO_4,22H_2O$$
is formed.

This salt, which occurred as the solid phase, but was not separated from adhering solution, was seen to consist, as mentioned by Apjohn, of fine, needle-shaped crystals, with a peculiar property of knotting up into masses not unlike tapioca.

It is submitted that the term " pseudo-alum " should not be applied to this salt, which shows no resemblance to the alums.

LXXVI.—*Interactions of Tellurium Tetrachloride and Acetic Anhydride.*

By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

DURING the last three years it has been demonstrated by a comprehensive series of experiments that tellurium tetrachloride condenses to form cyclic compounds with β-diketones (I) in their diketonic form, and accordingly the diketone may contain two alkyl substituents on the carbon atom 3 so long as the terminal carbon atoms 1 and 5 are present as methylene groups.

(I.) $\begin{matrix} R{\cdot}CH_2{-}CO \\ {}_5^1 \quad\quad {}_4^2 \; {}_3{>}CR'R''. \\ R{\cdot}CH_2{-}CO \end{matrix}$ (II.) $\begin{matrix} R{\cdot}CH_2{\cdot}CO \\ {>}O \\ R{\cdot}CH_2{\cdot}CO \end{matrix}$

(R, R', R'' are hydrogen atoms, or alkyl or arylalkyl groups.)

So far as these researches have been carried, it has been found that any diketone of general formula I furnishes a chelate group to tellurium and gives a *cyclo*telluripentanedione dichloride (III) which can be reduced quantitatively to the corresponding *cyclo*telluropentanedione (IV).

(III.) $Cl_2Te{<}^{CHR{\cdot}CO}_{CHR{\cdot}CO}{>}CR'R''$ $\rightarrow$ $Te{<}^{CHR{\cdot}CO}_{CHR{\cdot}CO}{>}CR'R''$ (IV.)

Since the foregoing processes may be regarded as general reactions, the 3-methylene group or its homologue plays no direct part in the condensation, and it appeared likely that this group

T 2

might be replaced by oxygen as in the aliphatic anhydrides (II). The experiment has been tried on acetic anhydride with the following results.

With tellurium tetrachloride and a large excess of acetic anhydride (6 mols.) in chloroform, condensation takes place and hydrogen chloride is evolved. The chief product is *dichlorotelluridiacetic acid* (V), a colourless, crystalline substance stable in moist air, m. p. 160—161° (yield 50% on $TeCl_4$), the production of which is probably consequent on the formation of a sensitive cyclic anhydride,

$$Cl_2Te{<}^{CH_2 \cdot CO}_{CH_2 \cdot CO}{>}O.$$
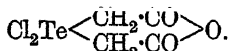
Reduction with alkali metabisulphite converts the dichloro-compound (V) quantitatively into *tellurodiacetic acid* (VI), a dichroic substance (pale yellow and colourless forms) exhibiting also dimorphism, m. p. 140—141°.

$$Cl_2Te{<}^{CH_2 \cdot CO_2H}_{CH_2 \cdot CO_2H} \quad \rightarrow \quad Te{<}^{CH_2 \cdot CO_2H}_{CH_2 \cdot CO_2H} \qquad {}^{Te \cdot CH_2 \cdot CO_2H}_{Te \cdot CH_2 \cdot CO_2H}.$$
$$\text{(V.)} \qquad\qquad\qquad \text{(VI.)} \qquad\qquad \text{(VII.)}$$
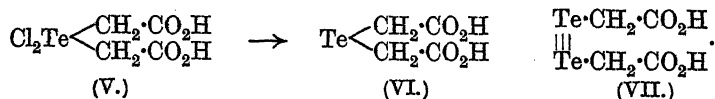
The discovery of the preceding telluro-compound (VI) completes the series $O(CH_2 \cdot CO_2H)_2$, $S(CH_2 \cdot CO_2H)_2$, and $Se(CH_2 \cdot CO_2H)_2$.

When exposed to moist air, tellurodiacetic acid is slowly oxidised in solution to amorphous oxytelluridiacetic acid. It is regenerated from this product by the action of bisulphite. Tellurodiacetic acid forms soluble yellow ammonium and sodium salts, whereas the white silver salt is amorphous and insoluble.

With $1\frac{3}{4}$ to 2 molecular proportions of acetic anhydride the condensation takes a different course and a grey flocculent solid separates from the concentrated chloroform solution. This deliquescent product, which consists probably of a mixture of trichlorotelluri-derivatives, $TeCl_3 \cdot CH_2 \cdot CO_2H$ and $(TeCl_3 \cdot CH_2 \cdot CO)_2O$, is reduced to *ditellurodiacetic acid* (VII), which separates in large, orange-red to ruby-red prisms, m. p. 144°, moderately soluble in water to a yellow solution.

The new acid forms soluble alkali salts and an orange silver salt which is photosensitive. From the final mother-liquors of this condensation separate colourless crystals of *methylene bistelluritri-chloride*, m. p. 173° (VIII).

$$CH_2{<}^{TeCl_3}_{TeCl_3} \quad \rightarrow \quad CH_2{<}^{Te}_{Te} \qquad CH_2{<}^{TeCl_2 \cdot CH_2 \cdot CO \cdot CH_3}_{TeCl_2 \cdot CH_2 \cdot CO \cdot CH_3}$$
$$\text{(VIII.)} \qquad\qquad \text{(IX.)} \qquad\qquad \text{(X.)}$$
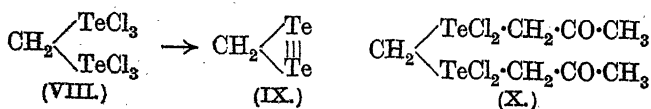
This substance, which no longer contains oxygen, is sensitive to moist air, becoming hydrolysed to oxychloride. It condenses

with acetone and other ketones to give well-defined, crystalline compounds such as *methylenebistelluriacetone dichloride* (X).

When reduced with bisulphite, methylenebistelluritrichloride loses all its chlorine and becomes converted into *ditelluromethane* (IX), a dark brownish-red, insoluble product changing slowly into a black powder, this alteration occurring rapidly at 40°; it explodes on heating more strongly. Ditelluromethane cannot be vaporised without decomposition and moreover it is insoluble in all the usual solvents. Hence its molecular complexity has not been ascertained. Probably both red and black varieties are polymerides, $(CH_2Te_2)_x$.* They react, however, towards chlorine or bromine to regenerate substances of the type $CH_2(TeX_3)_2$, where X is the halogen atom.

The acetic anhydride condensation has furnished other telluriferous by-products which together with the foregoing derivatives are still under examination.

The formation of a methylene compound (VIII) during these condensations is of considerable theoretical interest, since the production of the $-CH_2-$ group from acetic anhydride must involve a profound disruptive change, which would scarcely be anticipated in view of the mild conditions employed in the interactions. Methylenebistelluritrichloride may arise in one of the following ways :—

1. Scission of carbon dioxide and hydrogen chloride from trichlorotelluriacetic acid and tellurium tetrachloride :—

$$Cl_3Te \cdot CH_2 \cdot CO_2H + TeCl_4 = CH_2(TeCl_3)_2 + CO_2 + HCl.$$
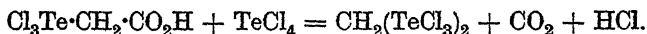
But for this decomposition there is little precedent.

2. Elimination of water and carbon suboxide from acetanhydrobistelluritrichloride :—

$$(Cl_3Te \cdot CH_2 \cdot CO)_2O \longrightarrow (Cl_3Te)_2CH_2 + H_2O + C_3O_2.$$
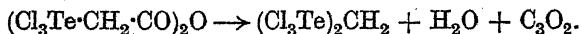
The brownish-red solutions from which methylenebistelluritrichloride is obtained suggest the presence of substances derived from carbon suboxide.

3. Intermediate formation of keten :—

$$CH_2{:}CO + 2TeCl_4 \longrightarrow CH_2(TeCl_3)_2 + COCl_2.$$
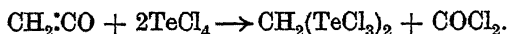
The reactions suggested under headings 2 and 3 require a dehydrating agent and tellurium tetrachloride would probably function in this way.

Attention should be directed to the development of colour among unsaturated tellurium derivatives. Tellurodiacetic acid, containing

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* The cyclic structure $CH_2{\overset{\diagup Te \cdot Te \diagdown}{\underset{\diagdown Te \cdot Te \diagup}{}}}CH_2$ for ditelluromethane accords with the above suggestion of polymerism, but so far there is no experimental evidence for or against a twofold complexity.

only one atom of tellurium, is colourless or yellow, *cyclo*telluro-pentanediones are yellow, whereas compounds having a junction of two tellurium atoms in their molecules are more intensely coloured, ditellurodiacetic acid is red, and ditelluromethane is red or black. These colour differences offer a useful guide to the chemical constitution of organotellurium compounds.

EXPERIMENTAL.

Dichlorotelluridiacetic acid (V).—The turbid yellow solution of 20 g. of tellurium tetrachloride, 48 g. of acetic anhydride, and 150 c.c. of dry chloroform, when heated under reflux, rapidly evolved hydrogen chloride, and, after 4 hours, the liquid, decanted from elemental tellurium, was diluted with chloroform and the clear reddish-brown solution concentrated until a flocculent precipitate of grey crystals separated. Several crops of this product were collected, amounting in all to 13 g. The freshly separated material was deliquescent, but when kept in a vacuum desiccator, which was occasionally open, the substance became stable to moist air and the melting point rose to about 159°. This compound dissolved in cold acetone diluted with chloroform and was obtained crystalline by fractional precipitation with petroleum (b. p. 40—60°). Further purification was effected by adding petroleum to its solution in ethyl acetate and chloroform, when the compound separated in transparent, colourless, compact prisms, m. p. with intumescence 160—161° : 0·1743 gave 0·0952 CO_2 and 0·0317 H_2O, C = 14·90, H = 2·04; 0·1936 and 0·1104 gave 0·1752 and 0·0996 AgCl, Cl = 22·39, 22·32; 0·2485 gave 0·1004 Te, Te = 40·40. $C_4H_6O_4Cl_2Te$ requires C = 15·17, H = 1·91, Cl = 22·41, Te = 40·29%.

The dichloride separated from ethyl acetate–chloroform–petroleum either with or without ethyl acetate of crystallisation depending on the proportion of this solvent in the medium. The crystals containing solvent separated as spear-shaped needles or as vitreous, acicular prisms. These forms when powdered commenced to melt below 100° and gradually lost solvent in the desiccator.

The dichloride was insoluble in petroleum or benzene, very slightly soluble in chloroform, but dissolved readily in ether, acetone, alcohol, or acetic anhydride; in hot water it passed into solution, but with hydrolysis.

The oily mother-liquor from the foregoing preparation yielded small quantities of (1) *methylenebistelluritrichloride*, (2) a substance, not yet identified, forming colourless masses of woolly needles from acetone–benzene–petroleum, which intumesced at 152—153° and on reduction with aqueous metabisulphite yielded a red insoluble telluriferous product.

Tellurodiacetic Acid (VI).—When reduced with aqueous potassium metabisulphite (2·8 g. in 25 c.c.), dichlorotelluridiacetic acid (2 g.) gave with evolution of sulphur dioxide a pale yellow solution containing a suspension of grey needles. Repeated extraction of this product with small quantities of ether furnished tellurodiacetic acid in quantitative yield. This material crystallised from acetone-benzene in compact, yellow prisms or long, yellow needles; these specimens, when left in a desiccator, changed into a colourless modification dissolving in acetone to a yellow solution, from which the yellow forms were recovered. Both varieties melted at 140—141° with blackening : 0·1793 gave 0·1257 CO_2 and 0·0427 H_2O, $C = 19·13$, $H = 2·66$; 0·1903 gave 0·0978 Te, $Te = 51·39$. $C_4H_6O_4Te$ requires $C = 19·56$, $H = 2·46$, $Te = 51·92\%$.

Tellurodiacetic acid was readily soluble in water, alcohol, or ether, moderately soluble in ethyl acetate or acetone, but almost insoluble in benzene, chloroform, or light petroleum. Its solutions were pale yellow and from water or ethyl acetate it separated with solvent of crystallisation which in the latter case was held tenaciously. These solvated crystals were yellower and had a lower melting point.

Solutions of tellurodiacetic acid in water or ethyl acetate oxidised slowly to a colourless, amorphous, insoluble oxide, a change which was promoted by hydrogen peroxide but inhibited by a trace of sulphur dioxide. The acid blackened in presence of hydrochloric acid, but was stable to warm aqueous alkalis, and decomposed carbonates.

' The following salts were prepared : *diammonium* salt, sulphur-yellow powder decomposing at 135°, *disodium* salt, yellow, both soluble in water; *disilver* salt, white, amorphous, insoluble substance, stable to light; *copper* salt, light green precipitate.

When suspended in chloroform and treated with chlorine, tellurodiacetic acid reverted to dichlorotelluridiacetic acid.

Ditellurodiacetic Acid (VII).—A mixture of 10·4 g. of tellurium tetrachloride, 6·6 g. of acetic anhydride, and 70 c.c. of dry chloroform was heated under reflux for 4 hours, until the initially delayed evolution of hydrogen chloride had nearly ceased and the tetrachloride had dissolved. The clear orange-yellow solution, decanted from 0·2 g. of tellurium, was evaporated at the ordinary temperature in a vacuum desiccator to a viscid yellow oil which, when stirred with chloroform, gave a crop of grey, flocculent material. The product, weighing 3·3 g. after drying in a vacuum desiccator, melted indefinitely at 100° and was permanently deliquescent. It was never, however, quite homogeneous and consisted mainly of acetanhydrobistelluritrichloride, $TeCl_3 \cdot CH_2 \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot TeCl_3$,

which on exposure to moisture was transformed first to trichloro-telluriacetic acid, $TeCl_3 \cdot CH_2 \cdot CO_2H$, and then to hydroxylation products of this acid.

By reduction of this material with potassium metabisulphite (6 mols. to 1 mol. of anhydrobistrichloride), sulphur dioxide was evolved, and *ditellurodiacetic acid* was obtained in quantitative yield, partly precipitated and partly by ether extraction of the deep yellow solution. Purification was effected by crystallisation from acetone or acetone-benzene containing a little sulphur dioxide, when lustrous, orange-red to ruby-red prisms were obtained, which became discoloured at 140° and blackened at 144°: 0·1390 gave 0·0648 CO_2 and 0·0247 H_2O, C = 12·72, H = 1·99; 0·1546 gave 0·1054 Te, Te = 68·19. $C_4H_6O_4Te_2$ requires C = 12·87, H = 1·62, Te = 68·33%.

In water ditellurodiacetic acid was more sparingly soluble than tellurodiacetic acid, but the former dissolved more readily in ethyl acetate; it was also soluble in acetone or alcohol, but was insoluble in chloroform, benzene, or light petroleum. Ditellurodiacetic acid dissolved to orange or orange-red solutions, in which it became oxidised, on exposure, to an insoluble, amorphous oxide. It gave soluble, yellow alkali salts, a light green copper salt, and an orange silver salt, the last two being insoluble; the silver compound black-ened on exposure to light. When suspended in chloroform, it combined additively with chlorine or bromine, the bromide being a yellow solid.

The oily mother-liquor from the preparation of the foregoing trichlorotellurium compounds yielded 1 g. of methylenebistelluri-trichloride and a smaller amount of an unidentified substance (nacreous leaflets, m. p. 175° with decomp.) stable to moist air and giving a red telluriferous reduction product.

When in the preceding condensation the proportion of acetic anhydride was increased to 2 molecules and that of chloroform decreased to 4 c.c. per g. of tellurium tetrachloride, the deliquescent, grey solid obtained (6·5 g. from 18·5 g. of $TeCl_4$) melted near 130° and consisted of a mixture of di- and tri-chlorotellurium compounds, since on reduction it yielded only telluro- and ditelluro-acetic acids. This mixture contained Cl = 30·63 and Te = 41·88%, showing that the substance which by reduction furnished ditellurodiacetic acid must have one of the related formulæ, $TeCl_3 \cdot CH_2 \cdot CO_2H$ or $TeCl_3 \cdot CH_2 \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot TeCl_3$, the junction of two tellurium atoms occurring, therefore, on reduction.

Methylenebistelluritrichloride (VIII).—The chloroform filtrates from the above-mentioned grey solid, when concentrated and left in a vacuum, slowly deposited large, brittle, prismatic crystals

of almost pure *methylenebistelluritrichloride* (2·3 g.).   Recrystallised
from dry chloroform with exclusion of moist air, it separated in
colourless, transparent prisms, often of acicular habit, and melting
at 173° with effervescence and formation of a red liquid.   The
latter property distinguishes this substance from the other tellurium
compounds derived from acetic anhydride.   That this product
was not changed in composition by recrystallisation was shown
by the following data :   (i) original preparation :   0·1853 gave
0·0179 CO_2 and 0·0103 H_2O, C = 2·64, H = 0·62;   0·1004 gave
0·1782 AgCl, Cl = 43·91;   0·2207 gave 0·1179 Te, Te = 53·42;
(ii) recrystallised material :   0·4153 gave 0·0380 CO_2 and 0·0194 H_2O,
C = 2·50,   H = 0·52. $CH_2Cl_6Te_2$ requires   C = 2·49,   H = 0·42,
Cl = 44·16, Te = 52·93%.

Methylenebistelluritrichloride was slowly changed by moist
air with evolution of hydrogen chloride and hydrolysed immediately
by cold water to white, amorphous oxide or oxychloride.   Successive
treatment with aqueous caustic potash and nitric acid produced
an aldehydic odour.   The trichloride condensed readily with methyl
ketones.   ·

Methylenebistelluriacetone Dichloride (X).—When boiled under
reflux with chloroform containing a small proportion of acetone,
the preceding bistrichloride evolved hydrogen chloride and on
cooling the solution the diacetone condensation product separated
in quantitative yield.   Recrystallised from chloroform containing
acetone, the substance was obtained in lustrous, transparent,
colourless, prismatic needles, stable in moist air, m. p. 181°
(decomp.) :   0·1510 gave 0·0870 CO_2, 0·0333 H_2O, C = 15·72,
H = 2·47;   0·0724 gave 0·0790 AgCl, Cl = 27·00. $C_7H_{12}O_2Cl_4Te_2$
requires   C = 16·01,   H = 2·30,   Cl = 27·02%.   A similar crys-
talline condensation product was obtained with acetophenone and
accordingly it is likely that the reaction with ketones and allied
·compounds is capable of further extension.

Ditelluromethane (IX).—Finely-powdered methylenebistelluri-
trichloride (0·33 g. or 1 mol.) was mixed with 0·92 g. (6 mols.) of
potassium metabisulphite and 10 c.c. of cold water.   Sulphur
dioxide was evolved and *ditelluromethane* was produced as a dark
red, amorphous powder which, after washing with cold water, was
dried in a vacuum (yield quantitative).   This red substance changed
slowly at the ordinary temperature, but rapidly at or above 30°,
to a black modification which melted gradually from 50 to 90°
without decomposition, forming viscous, pitch-like drops.   On
cooling, this pitch resolidified to a dense, brittle solid having a
silvery lustre and resembling a heavy fusible metal.   This modifica-
tion was analysed :   0·1463 gave 0·0237 CO_2 and 0·0133 H_2O;

$C = 4.42$, $H = 1.02$; 0.1706 gave 0.1606 Te, Te $= 94.14$ (total 99·58). CH_2Te_2 requires $C = 4.46$, $H = 0.75$, Te $= 94.79$ %.

When heated to a high temperature in air, ditelluromethane exploded with a brilliant bluish-green flash, evolving garlic odours and leaving a residue of tellurium. Ditelluromethane was insoluble in water or organic media. When suspended in chloroform, it absorbed chlorine, regenerating methylenebistelluritrichloride, and combined with bromine to form a yellow bromide intumescing violently at 214°.

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        EDGBASTON.

LXXVII.—The Influence of Valency Direction on the Dissociation Constants of Dibasic Acids.

By CLAUDE HYMAN SPIERS and JOCELYN FIELD THORPE.

As the outcome of work described in numerous papers, the hypothesis has been advanced that the angle between any two valencies of a carbon atom can be profoundly altered in at least two ways :

(1) by altering the volume of the groups attached to the other two valencies ;

(2) by inclusion of these two valencies in a ring complex, the internal angle of which can be assumed to be fixed.

Until recently, the evidence adduced in support of this hypothesis has been purely chemical. For example, it has been shown that an alteration in valency direction brought about in the ways above mentioned influences the ease of formation and the stability of ring systems, e.g., of β-lactones (Bains and Thorpe, J., 1923, **123**, 2742), and also determines whether ring-chain tautomerism shall occur in certain cases (see ibid., p. 2865). In Part XI (J., 1924, **125**, 2524) of the series of papers on ring-chain tautomerism, Dutt and one of us have used a physical method to demonstrate the shifting of equilibrium between the tautomeric coloured and colourless forms of the fluoresceins and rhodamines, produced by alteration of valency direction. The work now described shows the effect of this alteration by another physical method.

The diminution of the angle produced in either of the above ways must tend to cause the approximation of the carbon atoms (a) and

(b), $\diagup\!\!>\!\!C\!\!<\!\!\psi\substack{\;)\,(a)\\\searrow C\,(b)}$ and of any groups attached to them. It has long been recognised that the primary and secondary dissociation constants of dibasic carboxylic acids are largely determined by the distance between the carboxyl groups; the greater this distance, the smaller the primary constant and the greater the secondary constant. The cases of the oxalic acid series and the geometrically isomeric maleic and fumaric acids may be quoted in illustration. It is at once apparent that an alteration of the angle between two valencies of an atom which forms one of a chain of atoms connecting two carboxyl groups will show itself by an alteration in dissociation constant. Malonic, succinic, and glutaric acids form a good series of derivatives which can be utilised in studying this effect. Table I gives the dissociation constants of various β-substituted glutaric acids, which have now either been determined or redetermined by us. It also shows the equilibrium reached when keto- or ring-hydroxy-acids of the types I and II are heated in aqueous potash to 145°.

(I.) $\substack{R\diagdown\\R^1\diagup}C\!\!<\!\!\psi\substack{\diagup CO\cdot CO_2H\\\diagdown CH_2\cdot CO_2H}$ $\qquad\qquad$ $\substack{R\diagdown\\R^1\diagup}C\!\!<\!\!\substack{\diagup C(OH)\cdot CO_2H\\\diagdown CH\cdot CO_2H}$ (II).

TABLE I.

	Substituent.	Calc. value of ψ.	Equilibrium mixture. % Keto.	% Enol.	$K_{25} \times 10^5$
1.	H,H	115·3°	100	0	4·69
2.	Me,H	112·5	—	—	6·00
3.	Et,H	?	—	—	5·29
4.	(CH₂)₄ (cyclopentane ring).	109·7	100	0	17·3
5.	Me,Me	109·5	100	0	19·8
6.	Me,Et	?	100	0	24·4
7.	Et,Et	?	38	62	33·9
8.	Pr,Pr	?	29	71	33·9
9.	(CH₂)₅ (cyclohexane ring).	107·2	0	100	33·4
10.	(CH₂)₆ (cycloheptane ring).	105·3	Behaviour intermediate between that of 4 and 9.		39·5

It will be seen that the introduction of *gem*-groupings causes a remarkably large increase in dissociation constant, ββ-dipropyl-glutaric acid being several times stronger than glutaric acid, whereas the variation in dissociation constant produced by introducing alkyl groups into the various fatty acids is nothing like as great, as can be seen from Table II.

<div align="center">

TABLE II.

$K_{25} \times 10^5.$

</div>

Formic acid	21·4				
Acetic acid	1·80				
Propionic acid	1·34				
n-Butyric acid	1·52	Dimethylacetic acid	1·43	Trimethylacetic acid	0·98
n-Valeric acid	1·50	Methylethylacetic acid	1·68	Dimethylethylacetic acid	0·96
n-Hexoic acid	1·38	Diethylacetic acid	1·95		
Heptoic acid	1·31	Ethylpropylacetic acid	1·97*		
		isoPropylacetic acid	1·67		

<div align="center">

* Determined by us.

</div>

Large increases of dissociation constant are also produced in the malonic and succinic acids by similar changes in structure (see below), but the hypotheses which have hitherto been advanced to explain the relationships between chemical constitution and acidity throw no light on the mechanism causing the large effects now discussed.   On the one hand, it is not yet possible to apply successfully modern electrical theories of valency and the structure of atoms and molecules, even to the most simple cases of substitution (compare Lewis, " Valence and the Structure of Atoms and Molecules," 1923, chap. VIII; Thompson, *Phil. Mag.*, 1923, [vi], **46**, 497). On the other hand, generalisations which have been deduced empirically without consideration of the inner structure of atoms and molecules present many difficulties.   Of the various attempts to explain the effects of substitution on these lines, Flürscheim's seems to have gained the greatest currency.   This author considers the effect of a substituent to be the result of the operation of three factors—the " polar," " quantitative," and " steric " factors— the magnitude of each of which can be estimated by independent experiments.   He claims to be able to predict whether a substituent will increase or decrease the dissociation constant of an acid into which it is introduced and also the order of magnitude of the effect. He predicts, for example, that methylethylacetic acid should be stronger than dimethylacetic acid but weaker than diethylacetic acid.   However, here the so-called " steric " factor, the value of which is estimated from esterification experiments, is much more important than the other two factors.   Since no explanation is offered as to how this steric influence is produced, the theory is of small utility, as it stands (compare Derick, *J. Amer. Chem. Soc.*, 1911, **33**, 1167).   The present theory suggests a mechanism whereby part, at least, of this steric effect is produced.

    The alkylated glutaric, malonic, and succinic acids will now be discussed in detail, although it should be pointed out that the present paper is mainly concerned with the remarkable effects produced by

gem-groupings. The introduction of *gem*-groups into malonic acid or into glutaric acid in the ββ-position leaves the symmetry of the molecule unaltered. There is thus no free rotation effect to be considered and the acids of each series are strictly comparable with one another. The same applies to succinic acid, although the symmetry of the molecule is modified slightly. The present theory must, in addition, apply where only one alkyl group is introduced, for, here also, a change in valency direction results. In the case of succinic acid, since the alkyl group is necessarily attached to the same carbon atom as a carboxyl group, there will doubtless be a marked free rotation effect. The effect of substitution will be considered under two heads :

(1) the " general " effect, the magnitude and sign of which are estimated from the monobasic acids, and

(2) the " approach " effect, which is mainly brought about by altered valency direction.

The Glutaric Acids.

On the whole, the same result is reached whether we arrange the different groupings according to the magnitude of their effects on the dissociation constant of glutaric acid or according to their influence in causing ring-chain tautomerism of the kind above indicated. From Table II we see that the introduction of alkyl groups into the β-position in propionic acid causes a slight rise in acidity, the effect of the methyl group being the greatest. That the glutaric acids with a *gem*-grouping should be so very much stronger than the monosubstituted acids and that the diethyl acid should be stronger than the dimethyl acid, although the monoethyl acid is weaker than the monomethyl acid, is remarkable evidence of the volume effect in altering valency direction. Dipropylglutaric acid is very slightly soluble in water, and from the results obtained it is difficult to say whether it is stronger than the diethyl acid. However, from the chemical evidence one would not expect a very great difference between the two acids. As was expected, *cyclo*-pentanediacetic acid is weaker than dimethylglutaric acid, although perhaps the difference is somewhat large. *cyclo*Hexanediacetic acid, contrary to expectation, is weaker than dipropylglutaric acid. The experiments of Ingold and Baker (J., 1923, **123**, 122) seemed to indicate that the *cyclo*heptane ring was less effective than the *cyclo*hexane ring in diminishing the tetrahedral angle; on the other hand, the electrical measurements suggest the reverse, as one would anticipate, were the *cyclo*heptane ring, like the *cyclo*hexane ring, to lie in one plane. These anomalies in the cyclic acids suggested the

desirability of attempting to estimate the effect of ring closure. For this purpose *cyclo*pentane- and *cyclo*hexane-carboxylic acids were compared with diethyl- and ethylpropyl-acetic acids.

$$\begin{matrix} CH_3 \cdot CH_2 \\ CH_3 \cdot CH_2 \end{matrix}\!\!>\!\!CH \cdot CO_2H \;\; 1 \cdot 95 \times 10^{-5}. \quad \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix}\!\!>\!\!CH \cdot CO_2H \;\; 1 \cdot 16 \times 10^{-5}.$$

$$CH_3 \diagdown \begin{matrix} CH_2 \cdot CH_2 \\ CH_3 \cdot CH_2 \end{matrix}\!\!>\!\!CH \cdot CO_2H \; 1 \cdot 97 \times 10^{-5}.$$

$$CH_2\!\!<\!\!\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH \end{matrix}\!\!>\!\!CH \cdot CO_2H \;\; 1 \cdot 32 \times 10^{-5}.$$
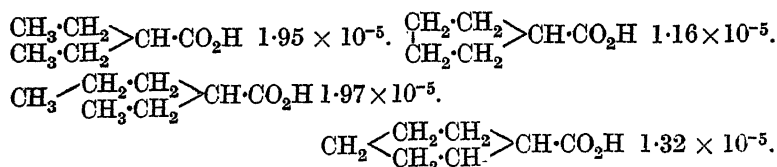
Thus ring closure in a simple acid causes a considerable decrease in dissociation constant, and this may explain why *cyclo*hexane-diacetic acid is weaker, instead of stronger, than dipropylglutaric acid; it may also explain the somewhat large difference in strength between *cyclo*pentanediacetic acid and dimethylacetic acid.

The Malonic Acids.

TABLE III.

$K_{25} \times 10^4.$

Malonic acid	16·3					
Methylmalonic	8·6					
Ethylmalonic	12·7	Dimethylmalonic	7·6			
n-Propylmalonic	11·5	Methylethylmalonic	16·1			
n-Butylmalonic	11·6	Methyl-*n*-propylmalonic	21·2	Diethylmalonic	74	
		Methyl-*n*-butylmalonic	20·3	Ethyl-*n*-propyl-malonic.	116	
				Ethyl-*n*-butyl-malonic.	116	
				Dipropyl-malonic.	119	

The introduction of one alkyl group has the same effect in malonic acid as in acetic acid—it acts as a positive group. A second small alkyl group also lowers the dissociation constant, but as the size of the alkyl group is increased the positive effect of the group is neutralised and reversed by the approximation of the carboxyl groups due to altered valency direction. The two *cyclo*paraffin dicarboxylic acids present an anomaly, for the acid with the larger ring is weaker than the acid with the smaller ring.

$$\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} CO_2H \\ CO_2H \end{matrix} \;\; 214 \times 10^{-4}. \quad CH_2\!\!<\!\!\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix} CO_2H \\ CO_2H \end{matrix} \;\; 8 \times 10^{-4}.$$
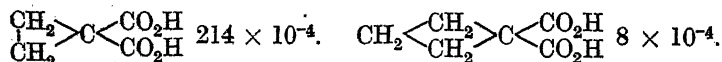
The substituent is here necessarily differently situated with respect to each of the two carboxyl groups. Table II shows that an alkyl group introduced in the α- or β-position into propionic acid causes a slight increase in acidity. Thus an alkyl group may be expected to raise slightly the dissociation constant of either carboxyl group. The remarkable effect of the *gem*-dimethyl group is seen by comparing

TABLE IV.

```
                                 1. Succinic acid
                                       6·6
                                 2. Methylsuc-
                                    cinic acid
        11. s-Dimethyl-                8·6
            succinic acid  3. Ethylsuc-      5. αα-Dimethyl-
            12·3 }            cinic acid        succinic acid
            19·1 }               8·8                8·2
        12. s-Methyl-      4. n-Propylsuc-   6. α-Methyl-α-    7. Trimethyl-
            ethylsuccinic     cinic acid        ethylsuccinic     succinic acid
            acid.               8·8              acid '             30·7
            20·1 }                                9·5
            20·7 }
14. s-Diethylsuc-  13. s-Methyl                              8. Dimethyl-    10. Tetra-
    cinic acid         propylsuc-                               ethylsuc-        methylsuc-
                       cinic acid                              cinic acid       cinic acid
    24·5 }             27·1 }                                    55·6             31·4
    34·3 }             33·5 }
                                                            9. Dimethyl-n-
                                                               propylsuc-
                                                               cinic acid
                                                                 55·1
15. s-Dipropyl-
    succinic acid
       25 }
       29 }
```

NOTE.—The symmetrical acids exist in two forms.

acids 2 and 7, 3 and 8, 4 and 9, and 5 and 10 (Table IV). Two alkyl groups produce a greater effect when attached to two different carbon atoms than when attached to the same atom. The above tables show that increase in the size of the groups beyond a certain limit produces very little or no further effect; this limit is reached with the ethyl or propyl group.

EXPERIMENTAL.

No details of the preparations of the various acids are given, since these are to be found in the literature. The two acetic acids were prepared from the corresponding malonic acids; the propyl iodide required for ethylpropylacetic acid was made from propyl alcohol obtained by the catalytic reduction of allyl alcohol. The cyclopentane- and cyclohexane-carboxylic acids were prepared from the corresponding bromides by the Grignard reaction. These four acids were purified by repeated fractionation in a vacuum, the portions used in the measurements being collected over a range of less than 0·5°. The solid acids were crystallised until their melting points were at least as high as those recorded in the literature and were constant. After the dissociation constant had been determined, each acid was again crystallised or distilled and the constant redetermined; in no case was an appreciable difference found.

The initial solutions were prepared from the required amounts of the acids, and the dilutions were made in the cell. The conductivities were determined at 25° by the Kohlrausch method, no attempt being made to achieve a degree of accuracy beyond that attainable with the ordinary apparatus. The results are corrected

for the conductivity of the water used; this was in the neighbourhood of 1.5×10^{-6} reciprocal ohm.

Acid.	Dilution (litres).	No. of determs.	Limits of $K \times 10^5$.	Mean $K \times 10^5$.	Other determinations.
Glutaric	16–1024	7	4.66–4.71	4.69	4.71. Voermann, *Rec. trav. chim.*, 1904, 23, 265.
β-Methylglutaric	33.46–1070.72	6	5.97–6.05	6.00	5.93. Walden, *Z. physikal. Chem.*, 1891, 8, 433.
β-Ethylglutaric	32.56–1041.92	6	5.28–5.36	5.29	
ββ-Dimethylglutaric ...	31.33–1002.56	6	19.5–20.0	19.8	20.0. Walker, *Annalen*, 1896, 292, 146.
ββ-Methylethylglutaric.	31.53–1008.96	6	24.2–24.6	24.4	
ββ-Diethylglutaric	32–1024	6	33.7–35.0	34.4(33.9*)	
ββ-Dipropylglutaric ...	512–2048	3	32.7–34.2	(33.9*)	
*cyclo*Pentane-1 : 1-di-acetic	127.2–2035.2	5	17.0–17.6	17.3	
*cyclo*Hexane-1 : 1-di-acetic	256–1024	3	33.3–34.2	33.7(33.4*)	
*cyclo*Heptane-1 : 1-di-acetic	279.6–1118.4	3	38.9–40.2	39.5	
Diethylacetic	31.38–1004.16	6	1.92–1.97	1.95	2.03. Billitzer, *Monatsh.*, 1899, 20, 666.
Ethylpropylacetic	38.74–1239.68	6	1.94–2.01	1.97	
*cyclo*Pentanecarboxylic.	26.77–856.64	6	1.14–1.18	1.16	1.24. Zelinsky and Isgaryschev, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 1379.
*cyclo*Hexanecarboxylic .	64.91–1038.56	5	1.27–1.37	1.32	1.34. *Idem, ibid.*

* Mean of the values at dilutions 512 and 1024.

Zelinsky and Isgaryschev (*loc. cit.*) used unplatinised instead of platinised electrodes, owing to a wandering of the minimum. No difficulty was experienced by the present authors with platinised electrodes.

We are indebted to the Chemical Society for a grant which met part of the expense of this investigation.

LXXVIII.—*6-Chlorophenoxarsine.*

By EUSTACE EBENEZER TURNER, and ARTHUR BRAXTON SHEPPARD.

ONE of us, while working in 1918 with Sir William Pope, obtained from arsenic trichloride and diphenyl ether a condensation product (then called *As-* or 6-chlorophenoxarsine) to which formula II was assigned. This formula was subsequently adopted by Lewis, Lowry, and Bergeim (*J. Amer. Chem. Soc.*, 1921, 43, 890).

The present communication describes the synthesis of 6-chlorophenoxarsine by a method which establishes its constitution, namely, by the elimination of hydrogen chloride from o-*phenoxyphenyldichloroarsine* (I) :

(I.) (structure: Cl_2As, O) → (II.) (structure: O, $AsCl$)
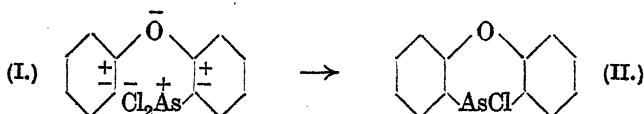
This conversion takes place with great readiness, for example, when one attempts to distil the dichloroarsine under diminished pressure. This result, surprising at first, is in full accord with the theory of alternate latent polarities, which, incidentally, appears to explain why Aeschlimann and McCleland (J., 1924, 125, 2025) failed to effect ring-closure with benzophenone-*o*-dichloroarsine (III) or the acid chloride (IV) of *o*-carboxydiphenylchloroarsine, and may also account for the comparative ease with which arsenic trichloride condenses with diphenyl ether, and the even greater ease with which it condenses with diphenylamine.

(III.) (structure: CO, Cl_2As)   (structure: $COCl$, $AsCl$) (IV.)
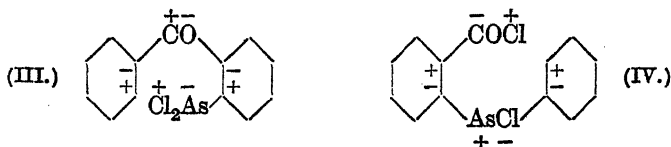
It seems justifiable to assume that in the above cases it is the element connecting the two benzene nuclei which acts as the key atom. In this connexion, it is important to note that arsenic trichloride and diphenyl ether do not interact in absence of aluminium chloride.

EXPERIMENTAL.

o-Nitrodiphenyl ether was prepared from *o*-chloronitrobenzene by a modification of the method used by Haeussermann and Teichmann (*Ber.*, 1896, 29, 1446). It was not found advantageous to use *o*-bromonitrobenzene, proposed by Ullmann (*ibid.*, p. 1878), whose method involves, also, the use of metallic potassium.

The liquid obtained by heating together potassium hydroxide (1 mol.) and water (0·6 mol.) was mixed with phenol (1 mol.) and a little copper powder, a mixture of phenol (1 mol.) and *o*-chloronitrobenzene (1 mol.) being added. The mixture was heated under reflux for 6 hours, the temperature being slowly raised from 150° to 210°. The cooled product was treated with water, extracted with ether, and the ethereal solution extracted with alkali. By evaporating the dried solvent, and distilling under diminished pressure, *o*-nitrodiphenyl ether was obtained in 85% yield.

o-Aminodiphenyl Ether.—Ullmann (*loc. cit.*), in preparing this compound by reduction of the nitro-compound with alcoholic stannous chloride, isolated the double tin salt and decomposed this

with hydrogen sulphide, apparently because Haeussermann and Teichmann (*loc. cit.*), using alkali to remove tin, were unable to isolate the amine. The following method, however, gave good results : the double tin salt, obtained by Ullmann's method, was dissolved in water, and treated below 0° with a large excess of potassium hydroxide. The resulting purple oil was extracted with ether, and the product distilled (b. p. 160—162°/12—15 mm.). The amino-compound, without further purification, melted at 41·5° (Found : N = 7·6; calc., N = 7·56%).

The *benzoyl* derivative forms white needles, m. p. 75° (Found : N = 4·9. $C_{19}H_{15}O_2N$ requires N = 4·84%).

o-*Phenoxybenzeneazo*-β-*naphthol*, obtained in the usual manner, separates from alcohol or glacial acetic acid in bright red needles, m. p. 135° (Found : N = 8·3. $C_{22}H_{16}O_2N_2$ requires N = 8·24%).

o-*Phenoxyphenylarsinic acid* and o-*phenoxyphenyldichloroarsine* were prepared as follows : The diazotised amine was slowly added to a well-stirred, ice-cold solution of arsenious oxide in sodium carbonate (usual proportions), a little copper sulphate being added at intervals. The temperature was finally raised to 50°, tar removed, and an excess of hydrochloric acid added. The arsinic acid separated as colourless needles. Owing to the small amount of material available, a little of the acid was collected, crystallised from water, and analysed (Found : M = 295, by titration with alkali. $C_{12}H_{11}O_4As$ requires M = 294), the acid suspension of the main bulk being saturated with sulphur dioxide in presence of a little iodine. The dichloroarsine separated as an orange-red oil, which was isolated by means of carbon tetrachloride. On attempting to distil it at 10 mm. pressure, it was completely converted into 6-chlorophenoxarsine, the colourless prisms obtained not depressing the m. p. (122°) of a specimen prepared from diphenyl ether and arsenic trichloride [Found : Cl = 12·7; As = 26·9; M (in boiling acetone) = 277. $C_{12}H_8OClAs$ requires Cl = 12·7; As = 26·9%; M = 279].

Note on the preparation of diphenyl ether. The preparation of the ether by the method described by Hirsch (*Ber.*, 1890, **23**, 3707; " Fortschritte," Friedlaender, III, 51) has been very fully investigated. Under no conditions was a yield of over 20% obtained, calculated on the aniline used.

Phenyl carbonate, heated under reflux with an equal weight of acetic anhydride for 14 hours, was quantitatively converted into phenyl acetate, no diphenyl ether being obtainable in this way : $(PhO)_2CO + Ac_2O = 2AcOPh + CO_2$.

Action of Aluminium Chloride on Diphenyl Sulphide [With H. S. BOLTON].—In an attempt to obtain the sulphur analogue of 6-chloro-

phenoxarsine, arsenic trichloride, diphenyl sulphide, and aluminium chloride (anhydrous) were heated together at 175—185°. Hydrogen chloride was evolved for some time, and the product was then cooled, treated with ice, then with hydrochloric acid, and extracted with ether. The latter contained only diphenylene disulphide (Found: C = 66·5; H = 3·7; calc., C = 66·7; H = 3·7%). When diphenyl sulphide was heated with aluminium chloride, benzene was obtained as one product, together with diphenylene disulphide, possibly formed as follows : (a) $SPh_2 + HCl = PhH + PhSCl$; (b) $2PhSCl = Ph·Ph + S_2Cl_2$; (c) $Ph·Ph + S_2Cl_2 = C_{12}H_8S_2 + 2HCl$. These changes are assumed to occur only in presence of aluminium chloride (compare Friedel and Crafts, *Ann. chim. phys.*, 1884, [vi], **1**, 530).

The Gas Light and Coke Company kindly supplied some of the o-chloronitrobenzene used in this investigation, and the authors desire to thank them and Mr. W. Gordon Adam of the Beckton Works for this gift.

EAST LONDON COLLEGE,
      UNIVERSITY OF LONDON.   *[Received, December 11th, 1924.]*

LXXIX.—*A Determination of the Melting and Transition Points of Potassium Dichromate.*

By PERCY LUCOCK ROBINSON, GEORGE EDWARD STEPHENSON, and HENRY VINCENT AIRD BRISCOE.

IN the course of another investigation, it was necessary to fuse recrystallised potassium dichromate in order to eliminate traces of organic matter, and our attention was thus drawn to the behaviour of the molten salt on cooling.

Mitscherlich (*Ann. Phys. Chem. Pogg.*, 1833, **28**, 120) stated that the crystals obtained from molten potassium dichromate, which he supposed to be identical with those separating from aqueous solution, " fall rapidly to a powder " on cooling. The change is so striking as to suggest immediately that a transition to another form has occurred, but we could find no description of the phenomenon in English text-books and thus were led to investigate the matter further. Lehmann (*Molekularphysik*, 1888, **1**, 172) observed the change under the microscope, and Wyrouboff (*Bull. soc. franç. min.*, 1890, **13**, 277), on the evidence of the change in extinction angle of the crystals on cooling, concluded that potassium dichromate existed in three forms, a " *clinorhombique* " form stable at temperatures near the melting point, a triclinic form stable at the ordinary temperature, and a second triclinic form stable within a narrow

range of temperature between its transition points into the other forms.   These transition points were not determined.

Tammann ("Kristallisieren und Schmelzen," 1903, p. 40) found that the breakdown of the crystalline solid occurred at a definite temperature, 240°, but without thermal effect.   Schemtschuschny (*Zeit. anorg. Chem.*, 1908, **57**, 267), in an account of the system $KCl-K_2Cr_2O_7$, gave 397° as the melting point and 236° as the transition point.

It is the purpose of this paper to record a description of the phenomenon accompanying the solidification and cooling of potassium dichromate and of a determination of the melting and transition points.

EXPERIMENTAL.

Fused potassium dichromate crystallises as a compact cake of large, dark brownish-red, tabular crystals, with a marked reduction in volume shown by the shrinkage of the still fluid portion into the interstices between the crystals, leaving a pitted surface on complete solidification.   On further cooling, the crystals change to a loose, orange-red powder, occupying a greater volume than the original solid.   Should the conditions be such that this change takes place before the whole of the melt beneath the crust has solidified, the expansion attending it often causes some of the fluid to well out in volcanic fashion through the crust.   The line separating the orange border and the dark compact mass is very sharp and obviously isothermal in character, as it conforms to the shape of the containing vessel.

The sharpness of the change is readily demonstrated by gathering the liquid on the end of a glass rod, allowing it to set, and, when the first signs of transition show at the edge, blowing gently upon it; the whole mass at once changes colour, breaks up, and falls off the rod.   This is so striking as to afford a good lecture experiment in illustration of transition between dimorphic forms, and if a thermometer be used in place of the rod an approximate indication of the transition temperature is obtained.

A similar experiment with fused anhydrous sodium dichromate shows neither colour change nor tendency to loosen from the rod; though this salt of course lightens in colour if kept at the ordinary temperature long enough to permit its hydration by atmospheric moisture.

The thermometric method was chosen as the readiest means of fixing more precisely the transition temperature of potassium dichromate.   As the expansion on cooling invariably burst glass test-tubes, the salt, which had been recrystallised, dried, and fused, was melted in a cylindrical copper vessel, heated electrically and

very well lagged. By suitably controlling the current supplied, any desired rate of cooling was attained. The thermometer was placed in a mercury bath contained in a narrow test-tube of stout glass immersed in the melt, and was thus protected from the compressive effect of this expansion, which could otherwise cause an apparent lag in temperature. Time intervals for each degree fall of the temperature were taken by means of two stop-watches, worked alternately, the thermometer being observed with a microscope. In this manner, a number of cooling curves for potassium dichromate and sodium dichromate were obtained. These made it apparent that sodium dichromate shows no arrest in cooling over the range 300—70°, while potassium dichromate shows a single well-marked arrest at 241° over a similar range.

The thermometer had been compared with a standard and the correction for exposed stem was applied.

As the transition temperature, 241°, is appreciably higher than Schemtschuschny's determination by use of a thermo-couple, it was decided to repeat the work using some other method of measurement. For this purpose a platinum resistance thermometer, in conjunction with a Callendar and Griffiths Bridge and a Hartmann and Braun moving-coil galvanometer, was substituted for the mercury-in-glass thermometer. The porcelain sheath covering the resistance element was immersed directly in the molten salt, contained in this case in a stout glass tube. The scale was arranged so that one division of the galvanometer scale, which could be read to tenths of a division, was equivalent to about 0·7°. To observe the rate of fall in temperature, the time taken for the light-spot to move over a division was measured, using two stop-watches as before. At the arrests, however, the resistance of the platinum was balanced against the bridge by bringing the light-spot to the previously noted zero point on the scale.

In this manner, the results obtained were (a) for the melting point 398·4° ± 0·5° (mean of five determinations) and (b) for the transition point 236·8° ± 0·5° (mean of seven determinations).

These results are accepted as correct to the exclusion of those obtained with the mercury thermometer.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
    NEWCASTLE-UPON-TYNE.

LXXX.—*The Reactivity of Antimony Halides with certain Aromatic Compounds. Part II.*

By ERNEST VANSTONE.

THE investigation by thermal analysis of binary systems containing antimony halides provides a useful method of tracing the conjugation of the residual affinity of unsaturated atoms or groups with that of the phenyl groups in compounds of the type Ph·α·α·Ph (J., 1914, **105**, 1491). The behaviour of certain compounds of the type Ph·α·β·Ph has now been investigated. The present paper deals with the systems (1) antimony trichloride–benzanilide, (2) antimony tribromide–benzanilide, (3) antimony trichloride–benzylaniline, and (4) antimony tribromide–benzylaniline.

Most aromatic compounds containing one benzene nucleus combine with 2 mols. of antimony halides, *e.g.*, $2SbCl_3,C_6H_6$. *s*-Diphenylethane and azobenzene combine with 4 mols. of the antimony compounds. The systems with benzylaniline have behaved otherwise and given results quite different from those obtained with any of the systems so far investigated.

<div align="center">EXPERIMENTAL.</div>

Benzanilide and Antimony Halides (With W. G. MESSENGER).

The Systems (1) *Benzanilide–Antimony Trichloride*, (2) *Benzanilide–Antimony Tribromide.*—The pure substances are colourless; the mixtures were dark red in the liquid state and reddish-brown in the solid. The mixtures, the freezing points of which were determined as described in previous papers, could be made to solidify only by seeding with the solid phase.

The diagrams (Fig. 1) representing these systems consist of four branches and show that in each system two stable compounds are formed having the composition $2SbX_3,NHPh·COPh$ and $SbX_3,NHPh·COPh$, respectively. The maxima are at 33·3 and 50% of $SbCl_3$ and 99° and 112°, respectively. These temperatures are the melting points of the compounds. It will be observed that for the mixture containing 59·32% of benzanilide, the portion of the curve below the eutectic has been obtained.

The system containing the tribromide has only one maximum point, namely, at 50% and 116°, the melting point of the compound $SbBr_3,NHPh·COPh$. The other compound, $2SbBr_3,NHPh·COPh$, is unstable, decomposing before its melting point is reached.

The above diagrams show that benzanilide, a compound containing two benzene nuclei, behaves like a compound with one nucleus only. Its reactivity towards antimony halides is nearly

equal to that of toluene. This can be seen by comparing the compounds formed :

Toluene.		Benzanilide.	
Ph·CH$_3$,2SbCl$_3$	stable.	Ph·CO·NHPh,2SbCl$_3$	stable.
Ph·CH$_3$,SbCl$_3$	,,	Ph·CO·NHPh,SbCl$_3$	,,
Ph·CH$_3$,2SbBr$_3$	,,	Ph·CO·NHPh,2SbBr$_3$	unstable.
Ph·CH$_3$,SbBr$_3$	,,	Ph·CO·NHPh,SbBr$_3$	stable.

FIG. 1.

Mols. of benzanilide per 100.
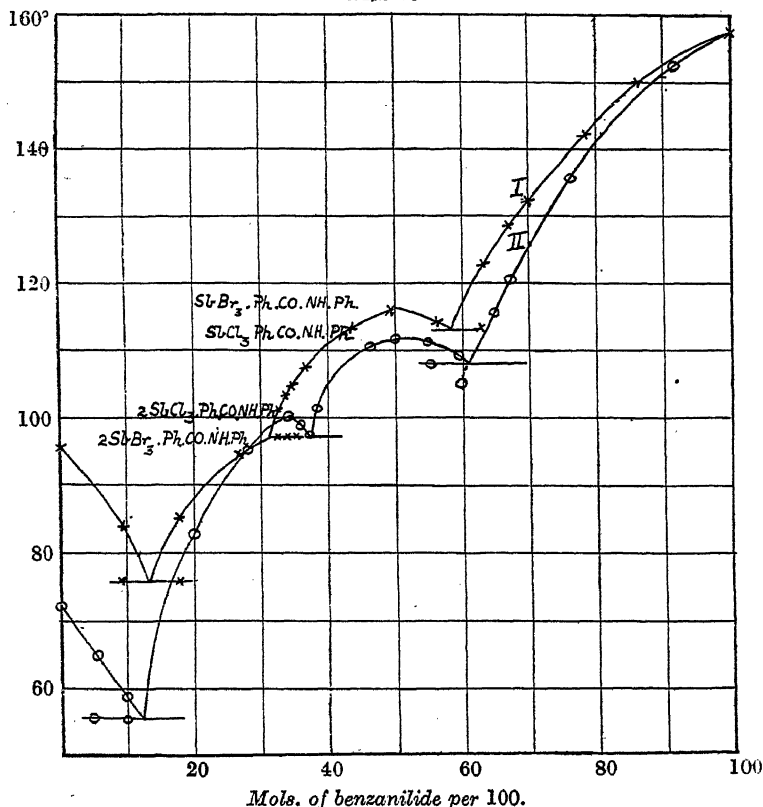
I *Antimony tribromide–benzanilide.*   II *Antimony trichloride–benzanilide.*

It is possible also to compare the reactivity of the groups Ph·CH$_2$·, Ph·NH·, and Ph·CO· with that of toluene, Ph·CH$_3$.

Group.	Combination with SbCl$_3$.	Combination with SbBr$_3$.
Ph·CH$_3$	Ph·CH$_3$,2SbCl$_3$	Ph·CH$_3$,2SbBr$_3$
	,, ,SbCl$_3$	,, ,SbBr$_3$
Ph·NH·	Ph·NH,2SbCl$_3$	Ph·NH,2SbBr$_3$ unstable
	,, ,SbCl$_3$	Ph·NH,SbBr$_3$
Ph·CH$_2$·	Ph·CH$_2$,2SbCl$_3$	Ph·CH$_2$,2SbBr$_3$
	,, ,SbCl$_3$	—
Ph·CO·	None	None

Systems containing Benzylaniline.

Benzylaniline–Antimony Trichloride and Benzylaniline–Antimony Tribromide.—The mixtures were dark green both in the liquid and the solid state.

The diagrams (Fig. 2) have three branches, showing the formation, in each system, of one stable compound only, having the composition $Ph\cdot CH_2\cdot NHPh,SbCl_3$ or $Ph\cdot CH_2\cdot NHPh,SbBr_3$.

FIG. 2.

Mols. of benzylaniline per 100.
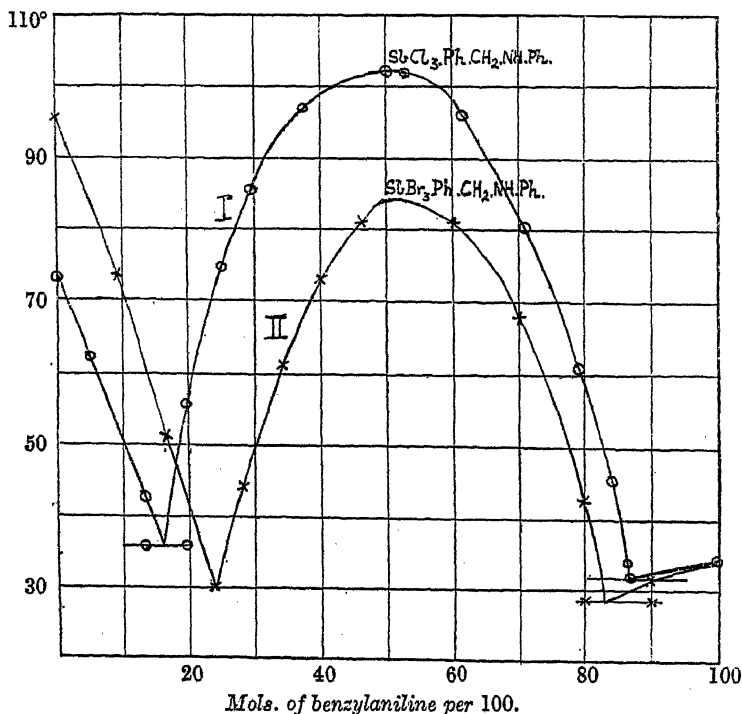
I *Antimony trichloride–benzylaniline.* II *Antimony tribromide–benzylaniline.*

Benzylaniline differs from the other similar aromatic compounds investigated in showing a greatly reduced reactivity towards antimony halides. No satisfactory reason can at present be assigned for this. Data for such optical properties as molecular refractive power which might throw light on the problem are not available.

SEALE-HAYNE AGRICULTURAL COLLEGE,
NEWTON ABBOT, DEVON.

LXXXI.—*The Cryoscopic Method for Adsorption.*

By HENRY LORIMER RICHARDSON and PHILIP WILFRID ROBERTSON.

THE adsorption of substances from solution has been investigated in the past only by methods involving filtration of the equilibrium mixture and subsequent estimation of the concentration of solute in the filtrate. There has been no general method for studying the adsorption of a variety of substances actually in the presence of charcoal in such a manner that increasing concentrations may readily be investigated.

Cryoscopy furnishes such a general method; it has been found that the adsorption of any substance soluble in the chosen solvent may be determined from its freezing-point depression curves, and that it is a simple matter to follow the rate of change of adsorption with concentration.

The solvent first chosen was water, in order that the accuracy of the method might be checked for a solute the adsorption of which could be determined by some quite independent method. Such a solute is acetic acid. The values for the adsorption ratio of acetic acid in charcoal and water (the ratio C_2/C_1), determined by the cryoscopic method at initial concentrations of $N/2$, $N/5$, and $N/10$, were 0·19, 0·44, and 0·85, whereas the corresponding values determined by the ordinary method of titration were 0·19, 0·44, and 0·86.

The Beckmann apparatus with magnetic stirrer was employed. Determinations were made with considerable care, and by adopting special precautions—notably the use of an intermediate cooling bath employing a cryohydric mixture—highly comparable results were obtained.

The water used as solvent was kept free from contamination by atmospheric carbon dioxide. The materials used as solutes were all scrupulously purified according to the best methods available in the literature. The charcoal was an acid-extracted animal charcoal of medium adsorptive strength, which was extracted by boiling water until neutral, and finally activated by heating to redness in a silica tube in a current of nitrogen. Its activity remained sensibly constant over the whole period of the operations, as was determined from time to time by the titration method with acetic acid.

In order to show exactly the method of calculation, the values for one solute—*n*-propyl alcohol—may be given in detail. In these determinations, 25 g. of water were used, and 2·5 g. of charcoal; two series of observations were made with increasing concentration

of solute : one series in the absence of charcoal, the other with charcoal present.

Without Charcoal.			*With Charcoal.*		
G. of solute added.	Total conc. of solute (g./100 g.).	Depression.	G. of solute added.	Total conc. of solute (g./100 g.).	Depression.
0·0350	0·1400	0·046°	0·0366	0·1464	0·020°
0·0420	0·3080	0·101	0·0359	0·2900	0·045
0·0763	0·6132	0·199	0·0872	0·6388	0·123

In Fig. 1, the curves AA″ and BB″ represent the depressions obtained with and without charcoal, respectively; the vertical lines

FIG. 1.

FREEZING-POINT DEPRESSION CURVES FOR

n-PROPYL ALCOHOL.

WITH CHARCOAL

Conc. (g./100 g.).
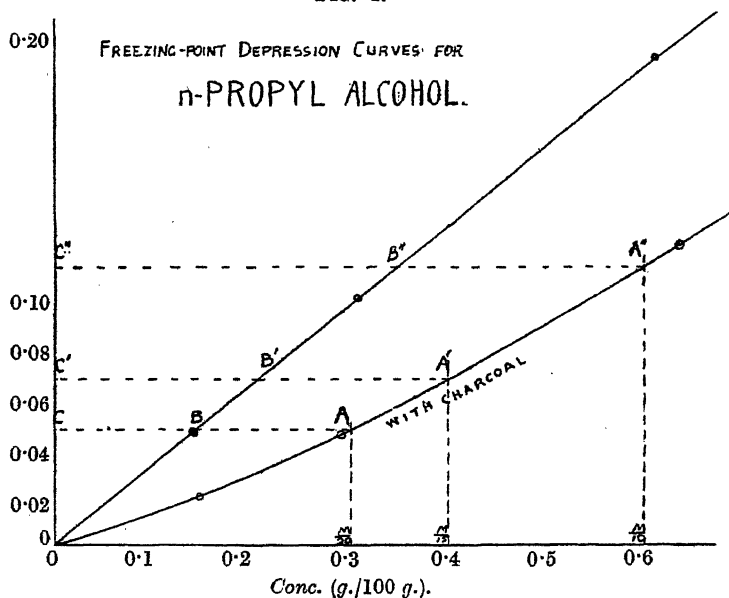
correspond with concentrations of $M/20$, $M/15$, and $M/10$. The distances AB, A′B′, and A″B″ give the concentration of solute in the charcoal (C_2), and the distances BC, B′C′, and B″C′, the concentration in the solute (C_1), for initial concentrations of $M/20$, $M/15$, and $M/10$, respectively.

The logarithms of C_1/MW and C_2/MW for the compounds examined are plotted in Fig. 2; from these curves may be obtained the magnitude of n in the formula $C_2 = KC_1^{1/n}$ (which is substantially accurate at low concentrations).

The following table summarises the results for the compounds examined, at an initial concentration of $M/20$; C_1 (in g. per 100 g.

of water) and C_2 (in g. per 10 g. of charcoal) were obtained from the freezing-point depression curves by the method given :

Substance.	$C_1.$		$C_2/C_1.$	$n.$
Methyl alcohol	0·126	0·034	0·25	2·3
Carbamide	0·216	0·085	0·39	1·4
isoPropyl alcohol	0·150	0·151	0·95	3·6
n-Propyl alcohol	0·143	0·158	1·10	1·9
Methyl acetate	0·133	0·237	1·76	2·4
Acetone	0·093	0·197	2·12	2·6
Sucrose	0·450	1·262	2·79	4·8
Acetic acid (by titration)	0·0758	0·226	3·00	—
Ether	0·049	0·321	6·5	2·3
Ethyl acetate	0·0375	0·403	10·8	3·1
Phenol	0·028	0·443	15·9	1·5
Pyridine	0·017	0·378	22·5	3·8
Aniline	0·015	0·450	30·0	2·6

The magnitude of the ratio C_2/C_1 places the compounds in the order of the points on the dotted line in the diagram (Fig. 2);

FIG. 2.

$$\frac{M}{20}$$

C_2

3·5   MOLECULAR
LOGARITHMIC CURVES
FOR
ADSORPTION FROM
AQUEOUS SOLUTION.
3·0

4·5   3·0   3·5 $\frac{M}{20}$ 2·0

Log. C_1.
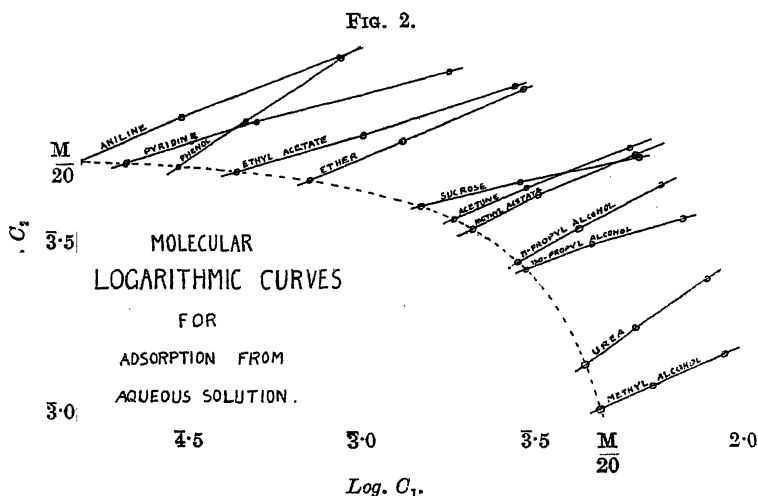
C_2/C_1, therefore, gives a measure of the relative adsorbability of a compound for a given initial concentration. The " constant " K has no comparative significance, as it is dependent both on the concentration and on the index, n.

The magnitude of n lies, in the compounds examined, between 1·45 and 4·8, varying thus around the mean value of 3, which was obtained by Freundlich for substances of widely differing types in aqueous solution. There is, furthermore, no apparent connexion between the value of n and the relative adsorbability C_2/C_1; and the latter factor appears to depend only vaguely on constitutive influences. Aromatic compounds are more readily adsorbed than

aliphatic, and, generally, molecular complexity tends to increase the adsorbability of a compound.

The second substance chosen as solvent in the cryoscopic study of adsorption was phenol. With a sample of phenol rigorously purified and freed from water, measurements were carried out with the following solutes : methyl alcohol, stearic acid, methyl succinate, water, and benzene. In every instance, the adsorption was nil, even for a compound of some complexity such as stearic acid. This completely negative result is surprising, although in agreement with the generally recognised fact that compounds which are readily adsorbed, as solvents prevent adsorption.

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      NEW ZEALAND.   [*Received, January 24th*, 1925.]

LXXXII.—*Substitution in Resorcinol Derivatives. Part I. Nitration of Derivatives of β-Resorcylaldehyde.*

By MYSORE GURU SRINIVAS RAO, COLLURAYANA SRIKANTIA, and
        MYSORE SESHA IYENGAR.

THIS communication, which deals with the nitration of 2-hydroxy-4-methoxybenzaldehyde [4-methoxy-β-resorcylaldehyde *] (Srinivas Rao and Sesha Iyengar, *Perf. Essent. Oil Rec.*, 1923, **14**, 300) and its derivatives, is a contribution to the study of the position taken by an entering group in polysubstituted benzenes.

β-Resorcylaldehyde on nitration gives 5-nitro-β-resorcylaldehyde (Gattermann, *Annalen*, 1907, **357**, 313, 383) and the corresponding acid (Hemmelmeyer, *Monatsh.*, 1904, **21**, 45; 1905, **26**, 185). Perkin (J., 1902, **81**, 1056), while working with brazilin, showed that the nitro-acid isolated from his nitrated mother-liquors was identical with that obtained by nitrating *p*-methoxysalicylic acid; he stated that it " probably is 5-nitro-acid." Bauer (*Ber.*, 1915, **48**, 509) nitrated 2 : 4-dihydroxyphenylarsinic acid and 4-hydroxy-2-methoxyphenylarsinic acid and in both cases found the nitro-group in position 5. In the nitration of salicylaldehyde the 3- and

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* Goulding and Pelly, who were the first to isolate this aldehyde from natural sources (P., 1908, **24**, 62; 1911, **27**, 235), have taken exception to one of our statements (*loc. cit.*) regarding its identity, as being " erroneous and misleading." The method by which they claim to have established the constitution of their new compound as 4-methoxy-β-resorcylaldehyde, *viz.*, by its conversion into β-resorcylic acid and resorcinol on fusion with potassium hydroxide (*Perf. Essent. Oil Rec.*, 1923, **14**, 370), cannot determine the position of the methoxy-group, for which, during the high-temperature reaction, a hydroxyl group was substituted.

the 5-nitro-aldehyde are both formed, the latter in the larger quantity (Mazzara, *Gazzetta*, 1876, 6, 460).

In nearly all these cases the nitro-group entered position 5. In the light of the theory that substitution is usually preceded by addition, 2-hydroxy-4-methoxybenzaldehyde should yield on nitration either the 3- or the 5-nitro-acid; probably the latter, if steric influences affect the entry of the nitro-group into position 3. The results obtained by previous workers and by us are quite in accord with this conclusion. We obtained good yields of the 5-nitro-compounds in all cases, but, owing to the minute quantities of solids obtained from the nitration mother-liquors, we have not yet been able to decide if the 3-nitro-isomeride also is formed, and if a nitro-group is substituted for the aldehyde group (Salway, J., 1909, 95, 1155; Harding, J., 1911, 99, 1585).

In all cases where two specimens are stated to be identical, the identity was proved by direct comparison and by the determination of the m. p. of a mixture of the two.

EXPERIMENTAL.

5-Nitro-2-hydroxy-4-methoxybenzaldehyde was obtained as a red, crystalline substance by nitrating 2-hydroxy-4-methoxybenzaldehyde in glacial acetic acid solution at 10—15° for 6 hours (yield 75—80%); a further quantity of less pure material was precipitated on diluting the acetic acid mother-liquor. Purified by reprecipitation from dilute sodium hydroxide solution with dilute sulphuric acid, and dried in a steam-oven, the substance became almost white and melted at 168—169°. It crystallised from benzene in round nodules and from chloroform and alcohol in needles, decomposed carbonates, gave a red colour with ferric chloride, and did not reduce alkaline silver nitrate solution. In the Zeisel estimation, the expulsion of methyl iodide proceeded slowly and was not complete even after 2 hours (this was the case also with all the other nitro-compounds described here) (Found : N = 7·5; OMe = 15·12. Calc. for $C_8H_7O_5N$, N = 7·1; OMe = 15·74%).

The yellow oxime melts at 215—216°, and the orange phenylhydrazone at 197—198°.

5-Nitro-2-hydroxy-4-methoxybenzoic acid, m. p. 228° (decomp.), can be obtained by oxidising the nitro-aldehyde with permanganate or by nitrating *p*-methoxysalicylic acid (Perkin, *loc. cit.*). Heated (0·5 g. with 10 c.c. of water) in a sealed tube for about 5 hours at 160—170°, it was nearly quantitatively converted into 4-nitroresorcinol 3-methyl ether, m. p. 143° (Weselsky and Benedikt, *Monatsh.*, 1880, 1, 887, give m. p. 144°) (Found : N = 8·5. Calc., N = 8·2%).

The nitro-group in the nitro-acid, and consequently in the nitro-aldehyde, is therefore in position 5. We tried to confirm this result by treating 5-nitro-β-resorcylic acid with methyl iodide and sulphate under different conditions, but methylation would not take place (compare Hemmelmeyer, *loc. cit.*), probably because of the presence of the *o*-nitro-group (compare Hewitt, Johnson, and Pope, J., 1913, **103**, 1628).

Methyl 5-Nitro-2-hydroxy-4-methoxybenzoate.—Methyl *p*-methoxy-salicylate was prepared by gradually treating 10 g. of β-resorcylic acid, dissolved in sodium hydroxide solution (3 parts), with the calculated quantity of methyl sulphate. After 12 hours, the alkaline mixture was distilled with steam, and 2·5 g. of the ester were obtained. It had a pleasant smell, melted at 49°, and gave a violet-red colour with ferric chloride.

This ester (1 g.), dissolved in a little glacial acetic acid, was warmed with 1 c.c. of nitric acid (*d* 1·42), and as soon as a vigorous reaction set in the mixture was cooled. The crystals which separated were filtered, washed with acetic acid, and recrystallised from methyl alcohol. The pink crystals obtained melted at 137—138°, gave a red colour with ferric chloride, dissolved freely in glacial acetic acid, but were sparingly soluble in alcohols. The sodium derivative is less soluble than the potassium derivative.

This nitro-ester was boiled with alcoholic potash for 2 hours; addition of dilute sulphuric acid to the solution precipitated 5-nitro-2-hydroxy-4-methoxybenzoic acid. Since the nitro-group in this acid is in position 5, that in the nitro-ester also should be in the same position.

5-Nitro-2 : 4-dimethoxybenzaldehyde.—2 : 4-Dimethoxybenzaldehyde (2 g.; obtained from methyl sulphate, sodium hydroxide, and 2-hydroxy-4-methoxybenzaldehyde) was dissolved in 8 c.c. of glacial acetic acid, 3 c.c. of nitric acid (*d* 1·42) were added, and the mixture was left in cold water for 12 hours. The pink needles which had separated were washed with a little acetic acid and crystallised from methyl alcohol; m. p. 188—189° (yield 75—80%).

The same nitro-compound was obtained by methylating 5-nitro-2-hydroxy-4-methoxybenzaldehyde in chloroform solution with methyl iodide and silver oxide. The yield was equally good, the solid was yellow and melted a degree higher.

The light yellow oxime melts at 184—185°, and the hydrazone, orange plates, at 169—170°. The nitro-aldehyde is sparingly soluble in alcohols, gives no colour with ferric chloride, and is insoluble in cold alkalis. If, however, it is boiled with alkalis, it gradually dissolves and a yellow solid of indefinite m. p. is precipitated on addition of dilute sulphuric acid to the cooled solution.

4-Methoxy-2-ethoxybenzaldehyde was prepared by ethylating 2-hydroxy-4-methoxybenzaldehyde in chloroform solution with ethyl iodide and silver oxide. The crude yellow solid was dissolved in ether, and the unchanged phenolaldehyde extracted with dilute caustic soda solution. The white solid finally obtained, m. p. 65—66°, was easily soluble in alcohols, chloroform, or acetic acid, insoluble in alkalis, volatile with steam, gave no colour with ferric chloride, and did not reduce silver nitrate solution readily. The pearly-white oxime melted at 95—96°, and the hydrazone, yellow plates, at 110—111°.

5-Nitro-4-methoxy-2-ethoxybenzaldehyde, m. p. 136—137°, obtained by nitrating the preceding aldehyde in the same way as methyl *p*-methoxysalicylate (above), is sparingly soluble in alcohols and more so in acetic acid or chloroform (Found : N = 6·34. Calc. for $C_{10}H_{11}O_5N$, N = 6·22%).

The same compound, m. p. 138—139°, was prepared by ethylating 5-nitro-2-hydroxy-4-methoxybenzaldehyde in chloroform with ethyl iodide and silver oxide. It did not give any colour with ferric chloride. Its yellow oxime melted at 185—186°, and the yellow hydrazone at 185—186°.

The nitro-compounds obtained by alkylating nitro-phenolic aldehydes by Purdie's method are usually yellow and melt a degree higher than those obtained by direct nitration of the dialkyloxy-aldehydes. The latter are red or brown, and melt quite sharply; repeated crystallisation does not improve either the colour or the m. p.

Preliminary Note on the Behaviour of 2-Hydroxy-4-methoxybenz-aldehyde.

This aldehyde, unlike its isomeride vanillin, is affected by moisture. It is converted by halogen acids (except hydrofluoric) into dark red solids, which are soluble in caustic alkalis and are reprecipitated by acids. The red substance produced by concentrated hydrochloric acid contains methoxy-groups but no halogen, and gives an acetyl derivative and a crimson bromo-derivative. Hot dilute phosphoric and sulphuric acids have no action on the aldehyde, but the cold concentrated acids slowly produce red solutions. On bromination in absence of sodium acetate, the aldehyde gives a red compound, probably formed by the action of the liberated hydrogen bromide.

2 : 4-Dimethoxy- and 4-methoxy-2-ethoxy-benzaldehyde are more soluble than 2-hydroxy-4-methoxybenzaldehyde in concentrated hydrochloric acid, and from the solutions violet and crimson amorphous solids are deposited.

Unlike the phenolic aldehydes and their ethers, the nitro-phenolic aldehydes and their ethers do not give coloured solids with hot concentrated hydrochloric acid.

There is no mention in the literature of this peculiar behaviour of these aldehydes, and it is being studied.

Like vanillin, 2-hydroxy-4-methoxybenzaldehyde may be used to detect traces of indole in cultures. Under equivalent conditions, it produces similar, but more delicate and less transient, colorations.

A New Indicator.   Vanillylidenenitromethane.

This compound (Knoevenagel, *Ber.*, 1904, **37**, 4502) can be used for colorimetric measurements of p_H-concentration within two ranges, namely, $p_H = 7$ to 8·5 and $p_H = 10$ to 11·5, being especially sensitive within the latter. A rough determination, kindly made for us by Mr. B. Sanjiva Rao, gave : $p_H = 2$—6, pale yellow; $p_H = 7$, pale pink; $p_H = 8$—10, pink; $p_H = 11$, pale pink; and $p_H = 12$, colourless. It is sensitive to carbonic acid, but gives sharp results with ammonia and mineral acids.

The indicator may be prepared by dissolving vanillin in absolute alcohol and adding the calculated quantity of nitromethane and a little ammonium carbonate. The long, deep yellow needles which separate after 2 days are washed with a little dilute sulphuric acid and with water.

CENTRAL COLLEGE, BANGALORE.   [*Received, September 29th,* 1924.]

LXXXIII.—*Syntheses of Substituted Succinic Acids containing Aromatic Residues.*

By WILSON BAKER and ARTHUR LAPWORTH.

THE method first used by Lapworth (P., 1904, **20**, 245) for the preparation of alkylsuccinic acids was worked out in detail by Lapworth and McRae (J., 1922, **121**, 1699) in the cases of phenyl- and piperonyl-succinic acids. Briefly, the method consisted in treating an aqueous solution of the sodium arylidenecyanoacetate, formed from the aldehyde and sodium cyanoacetate solution, with potassium cyanide, and hydrolysing the addition product to the substituted succinic acid, which, in the case of phenylsuccinic acid, was obtained in a yield of 65—70% calculated from the weight of benzaldehyde used.

Higginbotham and Lapworth (J., 1922, **121**, 49) showed that the maximum additions of the elements of hydrogen cyanide to

αβ-ethylenic linkings were obtained by treating the carboxylic esters, rather than the acids, with excess of potassium cyanide. It was therefore expected that by using the esters of the arylidene-cyanoacetic acids instead of their salts the addition of alkali cyanide would take place more readily and that better yields of the succinic acids would be obtained. This expectation has been fully realised, excellent yields of the succinic acids being obtained, except in those cases where specific difficulties of isolation of the acid (see vanillyl-succinic acid) or of hydrolysis of the addition product (see piperonyl-succinic acid) occurred.

Except in cases where an *o*-hydroxyl group is present, the arylidenecyanoacetic acids are completely esterified by boiling with alcohol containing a little anhydrous hydrogen chloride, and these esters readily react with sodium cyanide with evolution of heat, the products on hydrolysis giving the arylsuccinic acids. In the case of phenylsuccinic acid the yield from the benzaldehyde was 85% of the theoretical. In connexion with this preparation, it is interesting to note the influence which the α-cyano-group exerts on the reactivity of the double bond towards sodium cyanide; thus, whilst the above experiment indicated that the addition of sodium cyanide to benzylidenecyanoacetic ester must take place quantitatively and with great rapidity, since the yield of phenyl-succinic acid, calculated from the ester, was 95%, Higginbotham and Lapworth (*loc. cit.*) found that, in the case of cinnamic ester, the addition product gave on hydrolysis only a 20% yield of phenylsuccinic acid.

The attempted esterification of salicylidenecyanoacetic acid led to some interesting observations which have established the stereo-chemical formula of this acid, and possibly those of the arylidene-cyanoacetic acids in general.

By boiling a solution of the acid in alcohol with a small amount of anhydrous hydrogen chloride, a bulky, white solid was first produced which slowly dissolved, giving a solution of ethyl coumarin-3-carboxylate and a precipitate of ammonium chloride :—
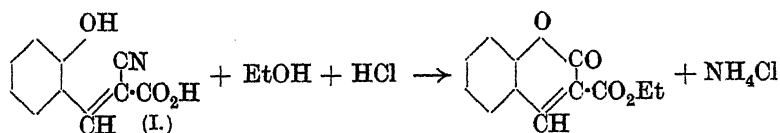
The insoluble solid consisted of free coumarin-3-carboxylic acid, either an imino-compound or ammonium coumarin-3-carboxylate, or perhaps both, and ammonium chloride.

It has been shown by several workers that salicylidenecyanoacetic acid is readily converted by the action of acids into coumarin-3-

carboxylic acid (see Haarmann and Reimer, D.R.-P. 189252).
Bechert (*J. pr. Chem.*, 1894, [ii], **50**, 11) suggested that hydrolysis
to salicylidenemalonic acid first took place, followed by lactone
formation, but this view is untenable owing to the great stability
of the nitrile group of the arylidenecyanoacetic acids (Lapworth
and McRae, *loc. cit.*, p. 1702), which is entirely unaffected during
the esterification of the carboxyl group, and also by prolonged boiling
with concentrated hydrochloric acid.

The formation of coumarin-3-carboxylic acid is now shown to be a
much more facile reaction than has hitherto been suspected. By
bringing salicylidenecyanoacetic acid and water to the boiling point
as quickly as possible, the yellow acid, itself insoluble in water, at
once forms a colourless solution of ammonium coumarin-3-carboxyl-
ate, which, on cooling and acidifying, deposits the free acid, m. p.
187—188°, in theoretical yield.   This reaction cannot be reconciled
with Bechert's view, or with the view that lactone formation first
takes place followed by hydrolysis of the 3-cyanocoumarin, since,
although the case of hydrolysis of 3-cyanocoumarin is not recorded
(see Bechert, *loc. cit.*), the corresponding amide, through which stage
the hydrolysis would necessarily proceed, is entirely unaffected
by many hours' boiling with water.

The authors hold that the only explanation of the reaction in
accordance with the facts is that the cyano-group condenses with the
o-hydroxyl group in the compound (I), forming an imino-compound
(II), probably having the structure of an internal salt, which is
immediately decomposed by water with formation of a solution of
ammonium coumarin-3-carboxylate (III) :—
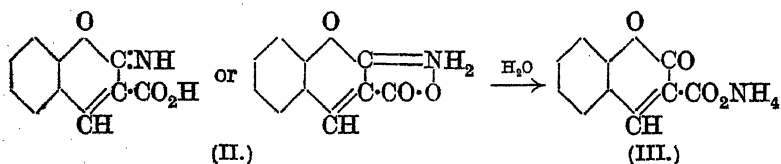
This view is further supported by the observation that by boiling
carefully dried salicylidenecyanoacetic acid with anhydrous alcohol,
it is converted into a white, insoluble substance, which dissolves
readily in cold water, giving a solution from which coumarin-3-
carboxylic acid is thrown down on acidifying.   This colourless com-
pound must be the imino-compound or its internal salt, since the
ammonium salt of the acid requires an additional molecule of water
for its formation.

Hence, owing to the remarkable ease with which the cyano-
group and the *o*-hydroxyl group interact, the acid must possess the

configuration in which these groups are adjacent, as shown in the formula (I).

This configuration, in accordance with the general nomenclature, is that of the "*trans*" acid, since the carboxyl and the hydroxyl group are not adjacent, and therefore do not form a lactone.

In contrast with the usual great stability of the nitrile groups of the arylidenecyanoacetic acids, Clarke and Francis (*Ber.*, 1911, **44**, 275) remark on the extraordinary ease with which the nitrile group of salicylidenecyanoacetic acid is hydrolysed with formation of coumarincarboxylic acid ("Cumarinsäure" is written instead of "Cumarincarbonsäure"). This apparently anomalous observation is at once explicable in the light of the above facts, since hydrolysis takes place, not of the cyano-group, but of the imino-group formed by its condensation with the *o*-hydroxyl group.

<center>EXPERIMENTAL.</center>

Esterification of the Arylidenecyanoacetic Acids.—The acids were all esterified under the same conditions, namely, by boiling the acid (25 g.) with alcohol (100 c.c.) containing anhydrous hydrogen chloride (3—4 g.) under reflux for 4 hours. The resulting solutions were filtered while hot and the esters crystallised out on cooling. The mother-liquors were concentrated and further small quantities obtained. The yields were all above 90% of those theoretically possible, and the esters were identical with those previously prepared from the aldehydes and ethyl cyanoacetate.

(1) *Phenylsuccinic Acid. Addition of Sodium Cyanide to Cyanophenylacrylic Ester.*—A mixture of cyanophenylacrylic ester (10 g.), alcohol (20 c.c.), and powdered sodium cyanide (5 g.) was gently heated on the steam-bath for 5 minutes, cooled, and water (200 c.c.) added. The resulting clear solution of the addition product was decomposed by hydrochloric acid, causing the precipitation of ethyl $\alpha\beta$-dicyano-β-phenylpropionate, $CHPh(CN)\cdot CH(CN)\cdot CO_2Et$, as a colourless oil, which, on standing, solidified to a mass of white crystals. (This compound, which has been described by Higson and Thorpe, J., 1906, 89, 1471, may be recrystallised from dilute methyl alcohol and obtained as colourless prisms, m. p. 64°).

Hydrolysis of the dicyano-compound. The ethyl $\alpha\beta$-dicyano-β-phenylpropionate was hydrolysed by boiling with concentrated hydrochloric acid (40 c.c.) for 4 hours. The solution, on cooling, deposited phenylsuccinic acid in small, white crystals, m. p. 165°, and a further small amount was obtained from the mother-liquor. The yield was 95% of that theoretically possible from the ester used.

(2) *Vanillylsuccinic Acid.*—Vanillylidenecyanoacetic acid was

prepared by Lapworth and McRae's general method (*loc. cit.*) by condensing vanillin (20 g.), dissolved in 10% sodium hydroxide solution (200 c.c.), at 60° with a solution of sodium cyanoacetate.

Addition of sodium cyanide to cyanovanillylacrylic ester and hydrolysis of the product. A mixture of cyanovanillylacrylic ester (25 g.), water (200 c.c.), and sodium cyanide (12·5 g.) was warmed on the steam-bath for ½ hour, when the original, intensely orange-yellow colour vanished.* The solution was concentrated till it became viscous, and the addition product hydrolysed by boiling with strong hydrochloric acid (100 c.c.) for 18 hours. The resulting solution of vanillylsuccinic acid and ammonium chloride was evaporated to dryness, and the former extracted with hot acetone, the solvent distilled off, and the dark residue dissolved in hot water (25 c.c.). On standing, vanillylsuccinic acid separated; the crystals were washed with a very little ice-cold water. By working up the mother-liquor the crude acid was obtained in 45% yield calculated from the weight of the ester used. The yield was poor owing to the extreme solubility of the acid in water, and attempts to isolate that remaining in solution as the carbethoxy-derivative (see below) resulted in uncrystallisable oils. It was recrystallised from water, then dissolved in boiling ether, and the filtered solution evaporated to a small bulk, when the acid crystallised in small, colourless crystals, m. p. 175—176° (Found : C = 54·85; H = 5·16; equiv. = 119·3. $C_{11}H_{12}O_6$ requires C = 54·98; H = 5·04%; equiv. = 120·1).

Vanillylsuccinic acid is readily soluble in water, ethyl alcohol, or acetone; almost insoluble in benzene or chloroform. It dissolves in aqueous sodium hydroxide, giving at first a colourless solution, which usually in a few seconds turns yellow and gradually, during a couple of minutes, assumes a reddish-pink colour, which is destroyed on acidifying, but reappears on making alkaline. In a solution of sodium carbonate the same phenomenon is observed, but the colour is less intense. These colorations are due to oxidation and the presence of the *p*-hydroxyl group, since if either oxygen is excluded, or the hydroxyl group is protected, no colour is observed. In an aqueous solution of the acid a minute trace of ferric chloride produces a bluish-green colour, but with slightly more of the reagent the colour

---

* The stages of the reaction are readily observed by treating the ester (5 g.) with 50% alcohol (30 c.c.) and sodium cyanide (2·5 g.), when the at first intensely orange-yellow solution of the sodium salt,

$$NaO \cdot C_6H_3(OMe) \cdot CH{:}C(CN) \cdot CO_2Et,$$
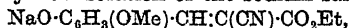
slowly deposits crystals, until in about 15 minutes a semi-solid yellow mass of the salt results. During the course of several hours this becomes more and more fluid, giving finally a clear solution of the sodium cyanide addition product.

lasts for only a fraction of a second and a brown solution results. This also is probably an oxidation phenomenon.

The *carbethoxy* derivative was obtained by the interaction of chloroformic ester and the acid in alkaline solution. It was precipitated on the addition of acid and recrystallised from ethyl acetate, being obtained in colourless crystals, m. p. 197—198° (Found : C = 53·72; H = 5·25; equiv. = 155·8. $C_{14}H_{16}O_8$ requires C = 53·82; H = 5·17%; equiv. = 156·1). It is easily soluble in alcohol or acetone, sparingly soluble in ether or cold water. It dissolves in a solution of sodium hydroxide without the formation of a pink colour, so long as the carbethoxy-group remains unhydrolysed.

Acetovanillylsuccinic anhydride, $\text{AcO·C}_6\text{H}_3(\text{OMe})·\overset{\displaystyle CO\text{———}O}{\text{CH·CH}_2·\text{CO}}$, was formed by boiling vanillylsuccinic acid with acetyl chloride. The crude product was washed with dry ether and recrystallised from chloroform–ligroin. It formed bunches of long, colourless needles, m. p. 112—113° (Found : C = 58·91; H = 4·44. $C_{13}H_{12}O_6$ requires C = 59·06; H = 4·58%). Acetovanillylsuccinic anhydride is readily soluble in chloroform, sparingly soluble in ether, and insoluble in ligroin.

(3) *Anisylsuccinic Acid,* $\text{MeO·C}_6\text{H}_4·\text{CH}(\text{CO}_2\text{H})·\text{CH}_2·\text{CO}_2\text{H}$.—The hydrolysis of the addition product of sodium cyanide to cyanoanisylacrylic ester proved to be more difficult than in the previous cases, since under similar conditions of hydrolysis, or by hydrolysing with alkalis, undesirable tarry products were obtained. The method finally adopted, which gave quite satisfactory results, was to treat the dinitrile in ethereal solution with anhydrous hydrogen chloride in the presence of alcohol, whereby the cyano-groups were converted into the imino-ether hydrochloride groups, –C(OEt):NH,HCl. The resulting substance was decomposed by water and was hydrolysed to the succinic acid by boiling with strong hydrochloric acid.

Addition of sodium cyanide to cyanoanisylacrylic ester and hydrolysis of the product. Cyanoanisylacrylic ester (5 g.), 50% alcohol (20 c.c.), and sodium cyanide (2·5 g.) were heated together on the steam-bath for 10 minutes. The resulting solution was diluted with water, acidified by hydrochloric acid, and the oily dicyano-compound extracted with ether. The extracts were dried, evaporated to about 25 c.c., alcohol (2 c.c.) was added, and the solution saturated at 0° with dry hydrogen chloride. Orange crystals, probably of the hydrochloride of the imino-ether, separated. After standing for 48 hours, the whole was hydrolysed by boiling with concentrated hydrochloric acid (100 c.c.) for 24 hours, when, on cooling, crude

anisylsuccinic acid separated. This product could not be satis-
factorily crystallised owing to the presence of a small amount of
tarry material, so the whole was evaporated to complete dryness,
and the solid residue repeatedly washed with ether in a Soxhlet's
apparatus until the filtrate was colourless. The remaining anisyl-
succinic acid was recrystallised from boiling water and obtained in
colourless, glistening, crystalline plates, m. p. 194—195°. The yield
was 70% of that theoretically possible calculating from the weight
of the ester used (Found : C = 58·93; H = 5·29; equiv. = 111·8.
$C_{11}H_{12}O_5$ requires C = 58·90; H = 5·40%; equiv. = 112·0).

Anisylsuccinic acid is readily soluble in methyl or ethyl alcohol
or acetone; almost insoluble in boiling benzene, ligroin or chloro-
form, or in cold ether.

Anisylsuccinic anhydride was prepared and recrystallised in the
same manner as acetovanillylsuccinic anhydride. It separated as
colourless, nacreous plates, m. p. 90·5° (Found : C = 63·69;
H = 4·87. $C_{11}H_{10}O_4$ requires C = 64·05; H = 4·89%). It is
easily soluble in chloroform or benzene, very sparingly soluble in
ether, and insoluble in ligroin.

(4) Piperonylsuccinic acid (Lapworth and McRae, *loc. cit.*) was
prepared in a manner similar to that used in making anisylsuccinic
acid, but the yield was poor owing to the production of tarry matter
during hydrolysis. It was best recrystallised by dissolving it in a
large bulk of boiling ether, and concentrating the solution, from
which it separated in small, colourless crystals.

Piperonylsuccinic anhydride, obtained and recrystallised in the
usual manner (see acetovanillylsuccinic anhydride above), formed
irregular, colourless crystals, m. p. 96° (Found : C = 59·76;
H = 3·73. $C_{11}H_8O_5$ requires C = 59·98; H = 3·66%). It is
easily soluble in chloroform, very sparingly soluble in ether or
benzene, and insoluble in ligroin.

Attempted Esterification of Salicylidenecyanoacetic Acid.—Since
salicylsuccinic acid has been prepared by Bredt and Kallen (*Annalen,*
1896, **293**, 366) by hydrolysis of the product of interaction of coumarin
and potassium cyanide, its preparation along similar lines to the
above was not attempted, but it was of interest to ascertain whether
salicylidenecyanoacetic acid could be esterified, since by condensing
salicylaldehyde with ethyl cyanoacetate only the " bis " product,
$OH·C_6H_4·CH[CH(CN)·CO_2Et]_2$, is obtained (Bechert, *J. pr. Chem.*,
1894, [ii], **50**, 11), and the same substance is also formed by the
action of ethyl cyanoacetate on salicylhydramide (Beccari, *Atti R.
Accad. Sci. Torino*, 1902, **37**, 137).

(a) *Preparation of ethyl coumarin-3-carboxylate.* Salicylidene-
cyanoacetic acid (5 g.) was boiled with alcohol (50 c.c.) containing

anhydrous hydrogen chloride (0·5 g.). After 1½ hours, the liquor was filled with a bulky, white solid, which gradually dissolved on further boiling, leaving a precipitate of ammonium chloride. The solution on standing deposited ethyl coumarin-3-carboxylate (3·6 g.) as colourless needles, m. p. 94°. This was identified by hydrolysis to the acid, m. p. 187—188°, and by comparison with a known specimen.

(b) *Formation of coumarin-3-carboxylic acid and its ammonium salt.* An experiment similar to the above was carried out, but the boiling was discontinued after 1½ hours. The white substance (2·7 g.) was filtered off and washed with cold alcohol. By treating with cold water, it largely dissolved, giving a solution which deposited much coumarin-3-carboxylic acid on acidifying. The residue insoluble in water was free coumarin-3-carboxylic acid, which, when recrystallised from dilute alcohol, melted at 187—188° (Found: C = 63·12; H = 3·33. $C_{10}H_6O_4$ requires C = 63·16; H = 3·18%).

THE UNIVERSITY, MANCHESTER. [*Received, December 11th, 1924.*]

LXXXIV.—*Ring-chain Tautomerism. Part XII. Derivatives of ββ-Dimethyl-α-ethylglutaric Acid.*

By GEORGE ARMAND ROBERT KON, LAURENCE FREDERICK SMITH, and JOCELYN FIELD THORPE.

THE work of Pandya and Thorpe (J., 1923, **123**, 2852) was undertaken with the object of studying the conditions of ring formation in derivatives of αββ-trimethylglutaric acid, which is to be regarded as the simplest member of the ββ-disubstituted acids having a substituent in the α-position; one of the objects of the research was also to settle the question of the type of tautomerism exhibited by the substance known as Balbiano's acid and, if possible, to prepare the latter synthetically. It was found, however, that there existed a marked tendency for halogen derivatives in this series to undergo fission under mild experimental conditions and to form monobasic acids of the acrylic series, and it was, therefore, impossible to prepare any substance having the properties of the acid obtained by Balbiano from camphoric acid. The great importance attached to the problem led us to investigate other α-substituted glutaric acids, and the α-ethyl acid, $CO_2H \cdot CHEt \cdot CMe_2 \cdot CH_2 \cdot CO_2H$, was chosen as the first for attack. This acid is readily obtainable by Kon and Thorpe's method (J., 1922, **121**, 1795).

It may at once be stated that the results now described emphasise Pandya and Thorpe's conclusions regarding the function of an

α-alkyl group in modifying the tendency to ring formation to which the complex is liable.

Thus, there appears to be but little tendency for the bromoderivatives of the α-ethyl acid to pass into derivatives of caronic acid, although we have isolated a certain quantity of a lactone which doubtless contains a trimethylene ring (VII) (see p. 569); there is also no evidence of the existence of ring-chain tautomerism between a keto- and a hydroxy-ring-acid such as is observed in glutaric acids without an α-substituent.

On the other hand, there is a very strong tendency, shared by derivatives of trimethylglutaric acid, for the whole molecule to undergo disruption with the formation of ββ-dimethyl-α-ethylacrylic acid (II), e.g., when the dibromo-acid (I) is treated with an alkaline hydroxide :

$$\text{(I.)} \quad Me_2C{\Large<}^{CEtBr\cdot CO_2H}_{CHBr\cdot CO_2H} \quad \longrightarrow \quad \text{(II.)} \quad Me_2C\!:\!CEt\cdot CO_2H + CO_2H\cdot CO_2H.$$
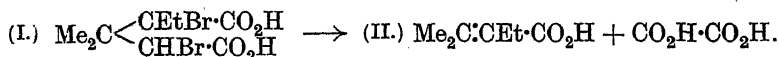
The formation of the acrylic acid in place of the expected trimethylene derivative may perhaps be an indication that the fission of the molecule precedes the elimination of hydrogen bromide, which then takes place with the production of the unsaturated acid. This view is rendered more probable by our observation that α-substituted glutaric acids are somewhat easily attacked even before they are brominated; in the process of hydrolysis leading to their formation from the alkylated Guareschi compounds (Kon and Thorpe, loc. cit.) they undergo fission to some extent, the alkylated portion of the chain being eliminated in the form of propionic or butyric acid, $>\!C{\Large<}^{CHR\cdot CO_2H}_{CH_2\cdot CO_2H}$.

Experiments were therefore made to discover under what conditions the α-ethyl acid suffered disruption, and it was found that treatment with concentrated potassium hydroxide for a short time is sufficient to produce considerable quantities of butyric acid and acetic acid. Boiling with 70% aqueous sulphuric acid produces a similar effect, butyric acid and small quantities of neutral substances being obtained. The cause of this remarkable change is at present still awaiting explanation, but is doubtless attributable to steric factors.

A feature of the α-ethyl acid is the fact that in spite of careful working it appears to be impossible to isolate any monobromoderivative under the usual conditions of the Hell-Volhard method of bromination, although the lactonic acid (III) (see below) must be formed from such a derivative.

Apart from these special features, the behaviour of the substances

investigated follows closely that of the trimethyl series, and the new compounds obtained in the course of the research need only be briefly mentioned.

When the dibromination product was esterified with alcohol, an acid fraction was always isolated, amounting to 30%. This consisted almost entirely of a lactonic acid analogous to that obtained in the trimethyl series and doubtless possessing the formula (III);* this substance was accompanied by a very small quantity only of an oil containing bromine and probably consisting of the monobromo-acid ester.

The neutral fraction consists of the $\alpha\gamma$-dibromo-ester, which, like many of its homologues, cannot be purified by distillation, as it is partly converted into the bromolactonic ester (IV) by loss of ethyl bromide.

$$\text{(III.)} \quad Me_2C{\begin{smallmatrix}CEt(CO_2H)\cdot O\\CH_2\text{------}CO\end{smallmatrix}} \qquad Me_2C{\begin{smallmatrix}CBrEt\text{------}CO\\CH(CO_2H)\cdot O\end{smallmatrix}} \quad \text{or}$$

$$Me_2C{\begin{smallmatrix}CEt(CO_2Et)\text{-}O\\CHBr\text{------}CO\end{smallmatrix}} \quad \text{(IV.)}$$
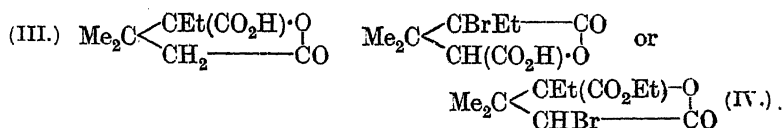
Hydrolysis of either the ester or the bromolactone with aqueous alkali causes fission as already mentioned, oxalic acid together with $\beta\beta$-dimethyl-α-ethylacrylic acid being the products. A very small quantity of an acid melting at 208° and possessing the formula $C_9H_{12}O_4$ was also isolated, but we were unable to prepare a sufficient quantity to establish its constitution.

The action of $5N$-methyl-alcoholic potassium hydroxide on the dibromo-ester leads to a hydroxy-lactone, m. p. 63°, having the formula V or VI, whereas the dibromo-acid (*cis* or *trans*) gives under the same conditions a lactonic acid, $C_9H_{12}O_4$, to which the constitution (VII) must be assigned, and which is quite similar to the compound isolated in the trimethyl series. Hydrolysis with $2N$-sodium carbonate leads to an inseparable mixture of the two isomeric hydroxylactonic acids (V and VI); analysis and titration results confirm this conclusion.

$$\text{(V.)} \quad CMe_2{\begin{smallmatrix}CEt(CO_2H)\cdot O\\CH(OH)\text{------}CO\end{smallmatrix}} \qquad CMe_2{\begin{smallmatrix}CEt(OH)\text{------}CO\\CH(CO_2H)\cdot O\end{smallmatrix}} \quad \text{(VI.)}$$

$$CMe_2{\begin{smallmatrix}CEt\text{------}CO\\C(CO_2H)\text{-}O\end{smallmatrix}} \quad \text{(VII.)}$$
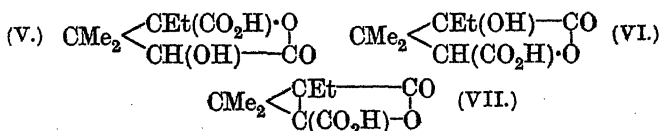
When the dibromination product was poured into anhydrous formic acid, a mixture of dibromo-acids was obtained which could be separated into two compounds by extraction with benzene, in which one proved to be sparingly soluble; when freed from its more

* The reasons for adopting this formula will be given in Part XIV.

soluble isomeride, it melted at 178° and was probably the *trans*-compound, whilst the second acid, to which the *cis*-configuration was assigned, melted at 145°. The action of hydrolysing agents on these acids was the same as on the dibromo-ester. If 80% aqueous formic acid was used in place of the anhydrous reagent, the solid isolated contained in addition to the dibromo-acids a considerable quantity of another substance, which melts at 154—155° and is the bromolactonic acid corresponding to the ester (IV); it gives the same products on hydrolysis with alkalis.

EXPERIMENTAL.

ββ-Dimethyl-α-ethylglutaric acid was prepared as described by Kon and Thorpe (*loc. cit.*), but it was found that the usual method of hydrolysis gave rather low yields, the acid being contaminated with butyric acid formed as the result of fission. Better results were obtained by boiling the imide for 3 hours with 60% acid (by volume), then diluting to 50%, and boiling for another 3 hours.

Fission of ββ-*Dimethyl-α-ethylglutaric Acid.*—The acid was boiled under reflux with an excess of 70% (by volume) sulphuric acid for 3 hours and distilled in steam; some 70% of unchanged initial material was recovered from the residue after steam distillation. The distillate, which smelt strongly of butyric acid, was extracted with ether, and the butyric acid removed by means of sodium carbonate and isolated as calcium salt. The ether extract on evaporation gave an oil, which partially solidified on keeping. The solid, on crystallisation from light petroleum, formed needles, m. p. 82°, probably consisting of a lactone, $C_7H_{12}O_2$ (Found : C = 65·30; H = 9·05. $C_7H_{12}O_2$ requires C = 65·61; H = 9·45%); it has not yet been investigated.

ββ-Dimethyl-α-ethylglutaric acid was heated with 8 times its weight of fused potassium hydroxide for 10 minutes. Water was then added and the acidified mixture distilled in steam. The distillate contained acetic and butyric acids, the latter being isolated as calcium salt (Found : Ca = 18·81. Calc., Ca = 18·73%). No unsaturated compounds appeared to be formed. About 70% of unchanged initial material was recovered.

Bromination of ββ-*Dimethyl-α-ethylglutaric Acid.*—The bromination was carried out exactly as described by Pandya and Thorpe (*loc. cit.*), thionyl chloride being used to form the acid chloride; the excess of this reagent was removed by warming under reduced pressure before the bromine was added.

Dibromination.—The neutral fraction, consisting of the ester of the acid I, decomposed on distillation; the analysis specimen was therefore purified by keeping in an evacuated desiccator for several

days and formed a viscous, yellow oil (Found : Br = 38·90. $C_{13}H_{22}O_4Br_2$ requires Br = 39·79%).

On distilling the oil under reduced pressure, it partially decomposed, the greater part of the distillate boiling at 184°/12 mm. and probably containing some of the bromolactonic ester IV together with unchanged dibromo-ester (Found : Br = 35·03%) ; a pure compound was not isolated from it.

The acid fraction, obtained in about 30% yield, deposited a large quantity of a bromine-free solid, whilst the residual oil still contained bromine (Found : Br = 19·65. $C_{11}H_{19}O_4Br_2$ requires Br = 27·07%) and probably consisted of impure monobromo-acid ester. The solid crystallised well from benzene–light petroleum (b. p. 60—80°), forming large, irregular crystals, m. p. 97°, and consisted of the lactone III [Found : C = 57·94 ; H = 7·71 ; equiv. (monobasic) = 189·5. $C_9H_{14}O_4$ requires C = 58·08 ; H = 7·53% ; equiv. = 186].

cis- and *trans-αγ-Dibromo-ββ-dimethyl-α-ethylglutaric Acids* (I).— When the dibromo-acid chloride was poured into anhydrous formic acid (5 vols.) instead of alcohol, the solution slowly deposited a crystalline solid on evaporation. The solid was drained on a porous plate, purified by washing with cold benzene, and separated into two fractions by extraction with hot benzene. The insoluble portion crystallised from acetone–benzene in large, rhombic crystals, m. p. 178° (decomp.) ; it was assumed to be the *trans*-dibromo-acid by analogy with other acids of this series (Found : Br = 45·67. $C_9H_{14}O_4Br_2$ requires Br = 46·23%). The benzene solution was mixed with light petroleum (b. p. 60—80°), when a more soluble acid separated, which was doubtless the *cis*-dibromo-acid ; after several crystallisations from benzene and petroleum, it formed irregular, crystalline aggregates, m. p. 145° (decomp.) (Found : Br = 46·47%).

The mother-liquors from which the dibromo-acids had been obtained yielded on further dilution with light petroleum a solid which, on repeated crystallisation from acetone and light petroleum, formed large, transparent, rhombic crystals, m. p. 154—155°, and consisted of the bromolactone (IV) (Found : Br = 30·02. $C_9H_{13}O_4Br$ requires Br = 30·16%). This compound was the principal product when the dibromo-acid chloride was poured into 80% formic acid instead of the anhydrous reagent.

Monobromination.—All attempts to monobrominate ββ-dimethyl-α-ethylglutaric acid led to mixtures of dibromo-derivatives with unbrominated material. The amount of acid fraction obtained was high—usually 50%—and this was similar to that obtained in the dibromination, consisting almost entirely of the lactone, m. p. 97°. On pouring the monobromination product into formic acid, a

mixture of the original acid with its dibromo-derivatives was obtained.

Hydrolysis of the Dibromo-derivatives.—Action of dilute sodium carbonate. The dibromo-ester (30 g.) was boiled with 200 c.c. of 10% aqueous sodium carbonate, until the oil had completely dissolved (6 hours). The solution was cooled, extracted with ether, acidified, and again extracted; the dried extract gave an oil on evaporation which did not solidify and was purified by keeping in a vacuum for a fortnight; analysis showed that it was probably a mixture of hydroxy-lactones (Found : C = 53·61; H = 6·80; equiv. = 183 and 104. $C_9H_{14}O_5$ requires C = 53·45; H = 6·95%; equiv. = 202 and 101). A similar mixture was obtained from the dibromo-acids and the bromo-lactone on boiling with sodium carbonate.

Action of aqueous potassium hydroxide. The dibromo-ester (17 g.) was added in a thin stream to a boiling solution of 50 g. of potassium hydroxide in 28 c.c. of water. After boiling for a further 5 minutes, the solution was cooled, diluted, extracted with ether, strongly acidified with hydrochloric acid, and again repeatedly extracted with ether. The extract gave, on drying and evaporating, an oily residue which deposited a small amount of solid. This was purified by washing with dry ether and recrystallised from hot water, being obtained in sparkling plates, m. p. 208° (decomp.); the quantity was only sufficient for analysis (C = 59·01; H = 6·93. $C_9H_{12}O_4$ requires C = 58·83; H = 6·58%).

A further large quantity of solid was obtained on treating the residual oil from the separation of the above substance with light petroleum (b. p. 40—60°) and evaporating the solution so obtained. The solid crystallised well from water, forming small, rhombic prisms, m. p. 49·5°, and consisting of ββ-*dimethyl-α-ethylacrylic acid* (II) [Found : C = 65·70; H = 9·23; equiv. = 130. $C_7H_{12}O_2$ (monobasic) requires C = 65·61; H = 9·44%; equiv. = 128]. Oxalic acid also was produced in this reaction and was identified in the usual way in the aqueous mother-liquor.

ββ-Dimethyl-α-ethylacrylic acid and oxalic acid were also obtained when weaker alkali was used or when the dibromo-acids or the bromolactone was hydrolysed with strong or dilute alkali; hydrolysis of the supposed monobromo-ester also gave the same products.

Action of 5N-methyl-alcoholic potassium hydroxide. The dibromo-ester (10 g.) was poured in a thin stream into 30 c.c. of the boiling reagent, and the mixture boiled for 15 minutes. On working up in the usual way, an oil was obtained which partly solidified on keeping. The solid was drained on a porous plate and formed plates, m. p. 63°, on crystallisation from benzene and light petroleum (b. p. 40—

60°); it was doubtless one of the hydroxy-lactones (V and VI) (Found : C = 53·86; H = 6·96; equiv. with cold barium hydroxide = 201. $C_9H_{14}O_5$ requires C = 53·45; H = 6·95%; equiv.=202 and 101). No other crystalline substance could be isolated from the syrup accompanying the above lactone.

When the bromo-lactone or the dibromo-acids were hydrolysed in the same way, the product was an oil, from which a solid gradually separated. This was drained and purified by crystallisation from benzene and light petroleum (b. p. 40—60°); it formed plates, m. p. 80°, and consisted of the bridged lactonic acid VII (Found : C = 59·23; H = 6·70; equiv.=190 and 91. $C_9H_{12}O_4$ requires C = 58·83; H = 6·58%; equiv.=184 and 92); about 30% of ββ-dimethyl-α-ethylacrylic acid was also isolated from the more soluble portion of the product.

LXXXV.—Tautomerism of Amidines. Part V. Methylation of Glyoxalines by Diazomethane. Bromination of 4(or 5)-Phenylglyoxaline.

By WILLIAM GREENWOOD FORSYTH and FRANK LEE PYMAN.

THE results of methylating glyoxalines by methyl sulphate (J., 1924, **125**, 1431 and earlier) have now been supplemented by the use of diazomethane and of methyl sulphate in the presence of aqueous sodium hydroxide. They are as follows :

Methylation of 4(or 5)-R-Glyoxaline to :

$$\underset{CH\!-\!N}{\overset{CR\cdot NMe}{}}\!\!\!>\!CH \quad \text{and} \quad \underset{CR\!-\!N}{\overset{CH\cdot NMe}{}}\!\!\!>\!CH.$$
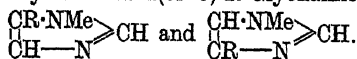
Proportions of 5 : 1/4 : 1-isomeride.

	Me_2SO_4.	Me_2SO_4 + NaOH.	CH_2N_2.
R = NO₂	350 : 1 †	0·33 : 1	45 : 1
Br *	45 : 1	1 : 1 ‡	10 : 1
Ph	0·2 : 1 †	— §	0·5 : 1

* In 2 : 4(or 2 : 5)-dibromo-5(or 4)-methylglyoxaline.
† J., 1924, **125**, 1431. ‡ J., 1910, **97**, 1814.
§ 4(5)-Phenylglyoxaline is insoluble in aqueous sodium hydroxide.

In the cases of both the nitro- and bromo-compounds the 5 : 1-derivative is a stronger base than the 4 : 1-derivative, and it will

be observed that in these two cases the more basic compound is formed almost exclusively by the use of methyl sulphate alone, and greatly predominates with diazomethane, whereas methyl sulphate and alkali yield as much, or more, of the 4 : 1 as of the 5 : 1-isomerides. The results harmonise with those obtained by von Auwers and his collaborators (1919—1922) by the alkylation of indazoles. Here also the stronger bases—the 2-alkyl derivatives—are obtained, generally almost exclusively, by methyl iodide alone, whereas the same reagent in the presence of sodium methoxide yields, as a rule, mixtures of the 1- and 2-alkyl derivatives, whilst in the one case where diazomethane was used the 2-derivative was obtained exclusively. Moreover, the feebler bases result as the main products on distillation of 1 : 2-dimethylindazolinium iodides (von Auwers) or of 1 : 3-dimethyl-4(5)-nitro(or -bromo)glyoxalinium iodides (J., 1924, **125**, 1431, 1564).

4(5)-Bromo-5(4)-methylglyoxaline, which was previously found to yield with methyl sulphate and aqueous sodium hydroxide the two isomerides with Br : NMe as 5 : 1 and 4 : 1 in the proportions 3 : 2 (J., 1910, **97**, 1814), has now been found to yield the first of these almost exclusively, when methyl sulphate is employed alone. Similarly, 4(5)-*bromo-5(4)-phenylglyoxaline* (I) yields with methyl sulphate alone, almost exclusively the isomeride with Br : NMe as 5 : 1, the constitution of the product VII being shown by its formation from 4-phenyl-1-methylglyoxaline (VIII) (J., 1924, **125**, 1431) on bromination. These results are consistent with the previous observations that with methyl salts 4(or 5)-bromoglyoxaline yields the 5 : 1- and 4 : 1-Br : NMe derivatives in the proportions 34 : 1 (J., 1924, **125**, 1564), whilst the 4(or 5)-methyl (J., 1922, **121**, 2616) and 4(or 5)-phenyl (J., 1924, **125**, 1431) groups act in the opposite way, yielding respectively 2·2 and 4·8 times as much of the 4 : 1- as of the 5 : 1-isomeride.

4(5)-Bromo-5(4)-phenylglyoxaline was obtained as the main product together with 2 : 4(2 : 5)-*dibromo*-5(4)-*phenylglyoxaline* (II) by the action of 1 mol. of bromine in chloroform on 4-phenyl-glyoxaline, and its formation falls into line with the results of bromination of other 4(5)-substituted glyoxalines (Me, J., 1910, **97**, 1814; PhNH·CO, King and Murch, J., 1923, **123**, 621), where also the derivatives with a single 5(4)-bromo-substituent were isolated in quantity, whereas glyoxaline and its 1- and 2-methyl derivatives are converted into the fully brominated tri- or di-bromo-derivatives under similar conditions with mere traces of less fully brominated glyoxalines (J., 1922, **121**, 947, 2626; 1924, **125**, 1564). The constitution of 2 : 4(2 : 5)-dibromo-5(4)-phenyl-glyoxaline follows from the fact that it gives benzoic acid on

oxidation, and therefore contains both bromine atoms in the glyoxaline ring, whilst that of 5(4)-bromo-4(5)-phenylglyoxaline is deduced from the facts (1) that it yields the above dibromo-compound on bromination, and (2) that it is not identical with 2-*bromo-4(5)-phenylglyoxaline*) III, which was synthesised by a method similar to that employed for 2-bromo-4(5)-methylglyoxaline (J., 1923, **123**, 494).

The crude ethyl α-aminobenzoylacetate hydrochloride resulting from the reduction of ethyl *iso*nitrosobenzoylacetate was condensed with potassium thiocyanate, yielding *ethyl 2-thiol-4(5)-phenylglyoxaline*-5(4)-*carboxylate* (IV), which gave on oxidation *ethyl 4(5)-phenylglyoxaline*-5(4)-*carboxylate* (V). Treatment of this base with bromine in cold chloroform gave, besides unchanged material, a product which was not obtained in a pure state, but must have been crude ethyl 2-bromo-4(5)-phenylglyoxaline-5(4)-carboxylate (VI). This gave on hydrolysis and decarboxylation 2-bromo-4(5)-phenylglyoxaline (III), in which the attachment of the bromine to the glyoxaline nucleus was proved by bromination to 2 : 4(2 : 5)-dibromo-5(4)-phenylglyoxaline.

$$\begin{array}{ccc}
\begin{array}{c}\text{CBr·NMe}\\ \text{CPh}\!-\!\text{N}\end{array}\!\!\!>\!\!\text{CH} & \longleftarrow & \begin{array}{c}\text{CH·NMe}\\ \text{CPh}\!-\!\text{N}\end{array}\!\!\!>\!\!\text{CH} \\
\text{(VII.)} & & \text{(VIII.)}
\end{array}$$

$$\begin{array}{cccc}
\begin{array}{c}\text{CBr·NH}\\ \text{CPh}\!-\!\text{N}\end{array}\!\!\!>\!\!\text{CH} & \longrightarrow & \begin{array}{c}\text{CBr·NH}\\ \text{CPh}\!-\!\text{N}\end{array}\!\!\!>\!\!\text{CBr} & \longleftarrow & \begin{array}{c}\text{CH·NH}\\ \text{CPh}\!-\!\text{N}\end{array}\!\!\!>\!\!\text{CBr} \\
\text{(I.)} & & \text{(II.)} & & \text{(III.)} \uparrow
\end{array}$$

$$\begin{array}{ccc}
\begin{array}{c}\text{EtO}_2\text{C·C}\!-\!\text{NH}\\ \text{CPh·N}\end{array}\!\!\!>\!\!\text{C·SH} \longrightarrow \begin{array}{c}\text{EtO}_2\text{C·C}\!-\!\text{NH}\\ \text{CPh·N}\end{array}\!\!\!>\!\!\text{CH} \longrightarrow \begin{array}{c}\text{EtO}_2\text{C·C}\!-\!\text{NH}\\ \text{CPh·N}\end{array}\!\!\!>\!\!\text{CBr} \\
\text{(IV.)} \qquad\qquad\qquad \text{(V.)} \qquad\qquad\qquad \text{(VI.)}
\end{array}$$
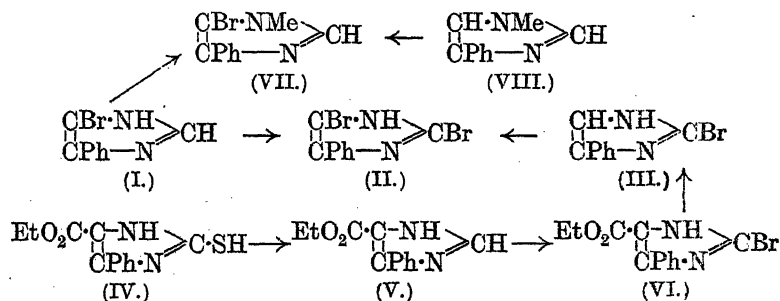
In the compounds I, II and III, the phenyl group exhibits a stabilising effect on the attachment of the bromine atoms (as also in 2-bromo-4 : 5-diphenylglyoxaline, J., 1924, **125**, 756), for these compounds are stable (or in the case of III fairly stable) towards 20% aqueous sodium sulphite at 100°, unlike the corresponding methylglyoxalines (J., 1923, **123**, 494), although they are reduced at higher temperatures.

EXPERIMENTAL.

Methylations by Methyl Sulphate.—2 : 5(2 : 4)-*Dibromo*-4(5)-*methylglyoxaline* (7·2 g.) and methyl sulphate (3·0 c.c.) reacted quickly when warmed; after the mixture had been heated for ½ hour in boiling water, aqueous sodium hydroxide was added and the mixture distilled with steam. The distillate gave on extraction

with ether 2 : 5-dibromo-1 : 4-dimethylglyoxaline (3·55 g., m. p. 41—43°, yield 55%),* and the residue gave on cooling 0·08 g. (yield 1·2%) of 2 : 4-dibromo-1 : 5-dimethylglyoxaline, m. p. 100—110°, which gave the pure substance on crystallisation from water, whilst the alkaline filtrate gave on treatment with hydrochloric acid and sodium carbonate 1·2 g. of 2 : 5(2 : 4)-dibromo-4(5)-methylglyoxaline, m. p. 212°.

5(4)-*Bromo*-4(5)-*methylglyoxaline* (10 g.) and methyl sulphate (6 c.c.) reacted immediately, the mixture being first cooled with water, and then heated in boiling water (10 mins.). After addition of aqueous sodium hydroxide (liquor L), ether removed an oil from which 5-bromo-1 : 4-dimethylglyoxaline was isolated as hydrogen oxalate (7·85 g., m. p. 96°, yield 55%), and in addition 1·8 g. of mixed bases were obtained. These were mixed with bromine (0·5 c.c.) in chloroform, and gave 2 : 5-dibromo-1 : 4-dimethylglyoxaline (1·1 g., m. p. 41·43°, yield 8%) and 2 : 4-dibromo-1 : 5-dimethylglyoxaline (0·01 g., m. p. 125°, yield 0·1%). The liquor L, when mixed with hydrochloric acid and sodium carbonate and extracted with ether, gave 1·85 g. of 5(4)-bromo-4(5)-methylglyoxaline, m. p. 153°.

5(4)-*Bromo*-4(5)-*phenylglyoxaline* (10 g.) and methyl sulphate (4·6 c.c.) reacted on warming, and after ½ hour at 100° the product was mixed with aqueous sodium hydroxide, when a white solid (8·5 g.) was precipitated. On extraction with hot light petroleum, 5(4)-bromo-4(5)-phenylglyoxaline (2·5 g., m. p. 228°) remained undissolved, whilst the extracted base gave pure 5-*bromo-4-phenyl*-1-*methylglyoxaline picrate* (11·42 g.; yield 73%). It forms fine, yellow needles, m. p. 226° (corr.), which are sparingly soluble in hot alcohol. (0·1315 gave 0·1984 CO_2 and 0·0319 H_2O. C = 41·2; H = 2·7. $C_{10}H_9N_2Br,C_6H_3O_7N_3$ requires C = 41·2; H = 2·5%). The same salt was isolated (yield 60%) from the product obtained by the action of bromine (1 mol.) in cold chloroform on 4-phenyl-1-methylglyoxaline. 5-*Bromo-4-phenyl*-1-*methylglyoxaline* crystallises from light petroleum in monoclinic prisms, m. p. 88—90° (corr.). (0·1095 gave 0·2025 CO_2 and 0·0389 H_2O. C = 50·4; H = 3·9. $C_{10}H_9N_2Br$ requires C = 50·6; H = 3·8%.)

Methylation by Methyl Sulphate and Sodium Hydroxide.—4(5)-*Nitroglyoxaline* (6 g.) in 10% aqueous sodium hydroxide (30 c.c.) was shaken with methyl sulphate (3 c.c.), cooling in water. A further 30 c.c. of aqueous sodium hydroxide and 3 c.c. of methyl sulphate were added, when 4-nitro-1-methylglyoxaline (2·3 g., m. p. 134°) separated; chloroform extracted a mixture from which

* In the experiments on methylation, yields are stated in percentages of the theoretical, allowing for recovered material.

0·65 g. of the same base, m. p. 134° (total yield 59%), was obtained after crystallisation from water. The filtrate from this gave 5-nitro-1-methylglyoxaline picrate (2·7 g., m. p. 153°, yield 19%), whilst the original alkaline liquor gave on acidification 1·0 g. of unchanged nitroglyoxaline.

Methylations by Diazomethane.—4(5)-*Nitroglyoxaline* (4·0 g.) was added to diazomethane in ether (50 c.c.) and washed down the condenser by methyl alcohol. Little obvious reaction took place, probably owing to the very sparing solubility of nitroglyoxaline in these solvents. After keeping over-night, no diazomethane remained, and the product gave 5-nitro-1-methylglyoxaline picrate (2·5 g., m. p. 153°, yield 58%), 4-nitro-1-methylglyoxaline (0·02 g., m. p. 134°, yield 1·3%), and recovered 4(5)-nitroglyoxaline (2·45 g.).

2 : 5(2 : 4)-*Dibromo*-4(5)-*methylglyoxaline* (8·0 g.) in methyl alcohol (40 c.c.) was added to diazomethane in ether (50 c.c.). Reaction took place immediately and after ½ hour no diazomethane remained. Separation of the products gave 2 : 5-dibromo-1 : 4-dimethylglyoxaline (1·5 g., m. p. 43°, yield 63%), 2 : 4-dibromo-1 : 5-dimethylglyoxaline (0·15 g., m. p. 126°, yield 6·3%), and recovered base (5·75 g., m. p. 215°).

4(5)-*Phenylglyoxaline* (10 g.) in methyl alcohol (50 c.c.) was added to diazomethane in ether (100 c.c.). Little reaction took place, and after 20 hours unchanged diazomethane was destroyed by the addition of acetic acid. Separation of the products gave 4-phenyl-1-methylglyoxaline picrate (3·8 g., m. p. 245°, yield 41%), 5-phenyl-1-methylglyoxaline picrate (1·85 g., m. p. 138—139°, yield 20%), and 4(5)-phenylglyoxaline nitrate (9·47 g., m. p. 174°).

Bromination of 4(5)-*Phenylglyoxaline.*—To 4(5)-phenylglyoxaline (20 g.) in chloroform (150 c.c.), one mol. of bromine (8 c.c.) in chloroform (40 c.c.) was added at 15° in ¾ hour. After removal of the solvent in a current of steam and addition of 500 c.c. of hot water, a mixture (A, 10·3 g.) separated. From the filtrate, sodium carbonate precipitated the monobromo-compound (17·5 g., m. p. 234°), whilst the mother-liquor, when acidified, concentrated, and mixed with sodium carbonate, gave 2·87 g. of 4(5)-phenylglyoxaline (m. p. 125°). Extraction of A with 5% aqueous sodium hydroxide left some monobromo-compound undissolved, and fractional precipitation of the solution with acid effected a partial separation of the mono- and di-bromo-compounds. After several repetitions of this treatment and crystallisation of the products from alcohol, there were obtained in the pure state 5(4)-bromo-4(5)-phenylglyoxaline (19·75 g., 64%) and 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline (4·56 g., 11%).

5(4)-*Bromo*-4(5)-*phenylglyoxaline* (I) crystallises from alcohol

stout needles, melting at 242—245° (corr.) to a brown liquid. It is insoluble in water and sparingly soluble in cold organic solvents. It is insoluble in aqueous ammonia or sodium carbonate, and only soluble with difficulty in hot aqueous sodium hydroxide. (0·1850 gave 0·3277 CO_2 and 0·0540 H_2O. C = 48·3; H = 3·3. 0·1737 gave 18·7 c.c. N_2 at 17° and 761 mm. N = 12·7. 0·1495 gave 0·1258 AgBr. Br = 35·8. $C_9H_7N_2Br$ requires C = 48·4; H = 3·1; N = 12·6; Br = 35·9%).

The *hydrochloride* crystallises from 5N-hydrochloric acid in long, silky needles, which contain $2H_2O$. On treatment with water or on heating, it yields the base. (0·1972, air-dried, lost 0·0236 in a vacuum over sulphuric acid. Loss = 12·0. 0·1463, air-dried, lost 0·0363 at 120°. Loss = 24·8. $C_9H_7N_2Br,HCl,2H_2O$ requires $2H_2O$ = 12·2; $2H_2O$ + HCl = 24·5%).

The *nitrate* crystallises from dilute nitric acid in fine, pale yellow needles, m. p. 127° (corr.). It dissociates on the addition of water. (0·1061 gave 0·1484 CO_2 and 0·0275 H_2O. C = 38·2; H = 2·9. $C_9H_7N_2Br,HNO_3$ requires C = 37·8; H = 2·8%.)

The *picrate* separates from alcohol in bright yellow needles, m. p. 188—189° (corr.). (0·1140 gave 15·1 c.c. N_2 at 18° and 763 mm. N = 15·6. $C_9H_7N_2Br,C_6H_3O_7N_3$ requires N = 15·5%.)

The base crystallised partly in the free state from an alcoholic solution containing 1 mol. of oxalic acid.

Bromination.—5(4)-Bromo-4(5)-phenylglyoxaline, on treatment with bromine (1 mol.) in chloroform at 18—20°, gave 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline (m. p. 197—198°, alone or mixed; yield 78%) together with 18% of unchanged material.

Action of Sodium Sulphite.—(1) *At* 100°. 5(4)-Bromo-4(5)-phenylglyoxaline (1 g.) was boiled with sodium sulphite (2 mols.) in 20% aqueous solution for 6 hours and filtered hot, when 0·94 g. was recovered unchanged. (2) *At* 170°. The base (3 g.) was heated with sodium sulphite (2 mols.) in 20% aqueous solution for 3 hours at 170°. After addition of hot water, 0·76 g. of unchanged material (25%), m. p. 235°, was collected, whilst the mother-liquor deposited, on basifying and cooling, 1·1 g. of 4-phenylglyoxaline, m. p. 128°, and gave on extraction with chloroform a further 0·02 g., m. p. 126°, the total yield being thus 57% of the theoretical. Both substances were identified by the mixed-melting point method.

2 : 5(2 : 4)-*Dibromo*-4(5)-*phenylglyoxaline* (II) crystallises from aqueous alcohol in rectangular prisms, melting at 198—199° (corr.) to a brown liquid. It is insoluble in water, readily soluble in alcohol or acetone, and somewhat sparingly soluble in other cold organic solvents. It is soluble in aqueous solutions of ammonia, sodium carbonate or hydroxide, but insoluble in 5N-hydrochloric or

sulphuric acid. (0·2050 gave 0·2685 CO_2 and 0·0412 H_2O. C= 35·7; H = 2·3. 0·1795 gave 14·4 c.c. N_2 at 19° and 761 mm. N = 9·4. 0·1361 gave 0·1689 AgBr. Br = 52·8. $C_9H_6N_2Br_2$ requires C = 35·8; H = 2·0; N = 9·3; Br = 53·0%). On oxidation with alkaline permanganate, it gave benzoic acid (yield 65%; m. p. 110°), which was purified and identified by the mixed-melting point method.

Action of Sodium Sulphite.—(1) *At* 100°. After boiling for 3 hours with 1 mol., and for 6 hours with 2 mols., of 20% aqueous sodium sulphite, 2 : 5-dibromo-4-phenylglyoxaline was recovered unchanged to the extent of 93 and 76% respectively.

(2) *At* 130°. The base (3 g.) was heated for 3 hours with 2 mols. of sodium sulphite in 20% aqueous solution. The product was dissolved in aqueous sodium hydroxide, and acidified with hydrochloric acid, when 1·88 g. (63%) were recovered unchanged, m. p. 196—197°. The mother-liquor gave on the addition of sodium carbonate 0·07 g. of crude 5-bromo-4-phenylglyoxaline, m. p. 225° (3%), and after concentration 0·34 g. of 4-phenylglyoxaline, m. p. 128° (24%). The three substances were identified by the mixed-melting point method.

Ethyl 2-Thiol-4(5)-phenylglyoxaline-5(4)-carboxylate (IV).—Ethyl *iso*nitrosobenzoylacetate was obtained by a modification of Perkin's method (J., 1885, 47, 244). To ethyl benzoylacetate (25 g.) in a little glacial acetic acid, sodium nitrite (10 g.) in saturated aqueous solution was added at 0°, when the *iso*nitroso-derivative separated (yield 97%) and gave 83% of the pure substance after crystallisation. This compound (10 g.) in 50 c.c. of alcohol was added slowly to 46 g. of hydrated stannous chloride in concentrated hydrochloric acid (100 c.c.) at 0°. The mixture was heated on the water-bath for ½ hour with 5 g. of tin foil, diluted with water, and freed from tin by means of hydrogen sulphide. After evaporation of the solvent under diminished pressure, there remained 7·7 g. of a greenish-white, semi-crystalline mass. This product, presumably the crude hydrochloride of ethyl α-aminobenzoylacetate, was dissolved in 20 c.c. of water, mixed with 5 g. of potassium thiocyanate in 10 c.c. of water, and heated in boiling water for 3 hours, when the thiolester separated; after crystallisation from alcohol, 4·8 g. were obtained in a pure state (40% of the theoretical yield, calculated on the *iso*nitroso-ester). The aqueous filtrate from the thiol-ester deposited some 2-thiol-4-phenylglyoxaline on concentration.

Ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate crystallises from alcohol in plates, m. p. 219° (corr.). It is insoluble in water, slightly soluble in cold alcohol, but readily soluble in chloroform and hot alcohol. (0·1291 gave 0·2742 CO_2 and 0·0587 H_2O. C = 57·ᵒ 5·1. $C_{12}H_{12}O_2N_2S$ requires C = 58·1; H = 4·1.

0·65 g. of the same base, m. p. 134° (total yield 59%), was obtained after crystallisation from water. The filtrate from this gave 5-nitro-1-methylglyoxaline picrate (2·7 g., m. p. 153°, yield 19%), whilst the original alkaline liquor gave on acidification 1·0 g. of unchanged nitroglyoxaline.

Methylations by Diazomethane.—4(5)-*Nitroglyoxaline* (4·0 g.) was added to diazomethane in ether (50 c.c.) and washed down the condenser by methyl alcohol. Little obvious reaction took place, probably owing to the very sparing solubility of nitroglyoxaline in these solvents. After keeping over-night, no diazomethane remained, and the product gave 5-nitro-1-methylglyoxaline picrate (2·5 g., m. p. 153°, yield 58%), 4-nitro-1-methylglyoxaline (0·02 g., m. p. 134°, yield 1·3%), and recovered 4(5)-nitroglyoxaline (2·45 g.).

2 : 5(2 : 4)-*Dibromo*-4(5)-*methylglyoxaline* (8·0 g.) in methyl alcohol (40 c.c.) was added to diazomethane in ether (50 c.c.). Reaction took place immediately and after ½ hour no diazomethane remained. Separation of the products gave 2 : 5-dibromo-1 : 4-dimethyl-glyoxaline (1·5 g., m. p. 43°, yield 63%), 2 : 4-dibromo-1 : 5-dimethyl-glyoxaline (0·15 g., m. p. 126°, yield 6·3%), and recovered base (5·75 g., m. p. 215°).

4(5)-*Phenylglyoxaline* (10 g.) in methyl alcohol (50 c.c.) was added to diazomethane in ether (100 c.c.). Little reaction took place, and after 20 hours unchanged diazomethane was destroyed by the addition of acetic acid. Separation of the products gave 4-phenyl-1-methylglyoxaline picrate (3·8 g., m. p. 245°, yield 41%), 5-phenyl-1-methylglyoxaline picrate (1·85 g., m. p. 138—139°, yield 20%), and 4(5)-phenylglyoxaline nitrate (9·47 g., m. p. 174°).

Bromination of 4(5)-*Phenylglyoxaline.*—To 4(5)-phenylglyoxaline (20 g.) in chloroform (150 c.c.), one mol. of bromine (8 c.c.) in chloroform (40 c.c.) was added at 15° in ¾ hour. After removal of the solvent in a current of steam and addition of 500 c.c. of hot water, a mixture (A, 10·3 g.) separated. From the filtrate, sodium carbonate precipitated the monobromo-compound (17·5 g., m. p. 234°), whilst the mother-liquor, when acidified, concentrated, and mixed with sodium carbonate, gave 2·87 g. of 4(5)-phenylglyoxaline (m. p. 125°). Extraction of A with 5% aqueous sodium hydroxide left some monobromo-compound undissolved, and fractional pre-cipitation of the solution with acid effected a partial separation of the mono- and di-bromo-compounds. After several repetitions of this treatment and crystallisation of the products from alcohol, there were obtained in the pure state 5(4)-bromo-4(5)-phenyl-glyoxaline (19·75 g., 64%) and 2 : 5(2 : 4)-dibromo-4(5)-phenyl-glyoxaline (4·56 g., 11%).

5(4)-*Bromo*-4(5)-*phenylglyoxaline* (I) crystallises from alcohol

Ethyl 4(5)-*Phenylglyoxaline*-5(4)-*carboxylate* (V).—The thiol-ester
(4·72 g.) was added gradually to 70 c.c. of gently-boiling 10% nitric
acid. When the effervescence had subsided, ammonia was added,
when 3·68 g. of ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate
separated in a pure state (yield 89%). It crystallised from alcohol
in needles, m. p. 225° (corr.). It is insoluble in water, and sparingly
soluble in ether. (0·1267 gave 0·3080 CO_2 and 0·0041 H_2O. C =
66·3; H = 5·7. $C_{12}H_{12}O_2N_2$ requires C = 66·7; H = 5·6%).

*Bromination Followed by Hydrolysis and Decarboxylation of the
Crude Bromo-ester.*—A suspension of 4 g. of ethyl 4(5)-phenylgly-
oxaline-5(4)-carboxylate in chloroform was mixed with 0·96 c.c.
of bromine diluted with chloroform. After a short time the mixture
was shaken with ammonia, when 1·08 g. of unchanged material
(m. p. 219°) separated. The chloroform solution was evaporated,
and the resulting oil was mixed with 30 c.c. of ether, when a further
0·42 g. (m. p. 211—220°) of unchanged material separated. The
ethereal mother-liquor gave on evaporation 3·46 g. of crude bromo-
ester as a light-brown gum. This substance (1·87 g.) was heated
with 20 c.c. of 25% sulphuric acid for 3 hours at 170°. The product
was basified with sodium carbonate and extracted with chloroform,
when 1·05 g. of red gum were obtained. This was extracted with
dry ether, which left the colouring matter mainly undissolved, and,
on concentrating the solution, 0·52 g. of 2-bromo-4(5)-phenyl-
glyoxaline crystallised in a pure state (yield 37% on the crude
bromo-ester).

2-*Bromo*-4(5)-*phenylglyoxaline* (III) crystallises from ether in
prisms, m. p. 153° (corr.). It is insoluble in water, and very easily
soluble in alcohol, ether, or chloroform. It is soluble in dilute
mineral acids or aqueous sodium hydroxide, but not in aqueous
sodium carbonate or ammonia. (0·0966 gave 0·1732 CO_2 and
0·0304 H_2O. C = 48·9; H = 3·5; 0·1266 gave 0·1066 AgBr.
Br = 35·8. $C_9H_7N_2Br$ requires C = 48·4; H = 3·1; Br = 35·9%.)

On treatment with bromine (1 mol.) in cold chloroform, it was
converted into 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline (yield
96%, m. p. 196—197° alone or mixed).

Action of Sodium Sulphite.—(1) *At* 100°. 2-Bromo-4(5)-phenyl-
glyoxaline (0·2 g.) was boiled with 2 mols. of sodium sulphite in
20% aqueous solution for 6 hours, and filtered hot from 0·14 g. of
partly unchanged material, m. p. 135—145°. The m. p. was raised
by the addition of 2-bromo-4(5)-phenylglyoxaline. The filtrate
gave a little 4(5)-phenylglyoxaline picrate on the addition of aqueous
cric acid. (2) *At* 150°. 2-Bromo-4(5)-phenylglyoxaline (0·2 g.)
heated with 5 mols. of sodium sulphite in 20% aqueous solution
3 hours at 150°. The product was extracted with chloroform,

sulphuric acid. (0·2050 gave 0·2685 CO_2 and 0·0412 H_2O. C= 35·7; H = 2·3. 0·1795 gave 14·4 c.c. N_2 at 19° and 761 mm. N = 9·4. 0·1361 gave 0·1689 AgBr. Br = 52·8. $C_9H_6N_2Br_2$ requires C = 35·8; H = 2·0; N = 9·3; Br = 53·0%). On oxidation with alkaline permanganate, it gave benzoic acid (yield 65%; m. p. 110°), which was purified and identified by the mixed-melting point method.

Action of Sodium Sulphite.—(1) *At* 100°. After boiling for 3 hours with 1 mol., and for 6 hours with 2 mols., of 20% aqueous sodium sulphite, 2 : 5-dibromo-4-phenylglyoxaline was recovered unchanged to the extent of 93 and 76% respectively.

(2) *At* 130°. The base (3 g.) was heated for 3 hours with 2 mols. of sodium sulphite in 20% aqueous solution. The product was dissolved in aqueous sodium hydroxide, and acidified with hydrochloric acid, when 1·88 g. (63%) were recovered unchanged, m. p. 196—197°. The mother-liquor gave on the addition of sodium carbonate 0·07 g. of crude 5-bromo-4-phenylglyoxaline, m. p. 225° (3%), and after concentration 0·34 g. of 4-phenylglyoxaline, m. p. 128° (24%). The three substances were identified by the mixed-melting point method.

Ethyl 2-Thiol-4(5)-phenylglyoxaline-5(4)-carboxylate (IV).—Ethyl *iso*nitrosobenzoylacetate was obtained by a modification of Perkin's method (J., 1885, 47, 244). To ethyl benzoylacetate (25 g.) in a little glacial acetic acid, sodium nitrite (10 g.) in saturated aqueous solution was added at 0°, when the *iso*nitroso-derivative separated (yield 97%) and gave 83% of the pure substance after crystallisation. This compound (10 g.) in 50 c.c. of alcohol was added slowly to 46 g. of hydrated stannous chloride in concentrated hydrochloric acid (100 c.c.) at 0°. The mixture was heated on the water-bath for ½ hour with 5 g. of tin foil, diluted with water, and freed from tin by means of hydrogen sulphide. After evaporation of the solvent under diminished pressure, there remained 7·7 g. of a greenish-white, semi-crystalline mass. This product, presumably the crude hydrochloride of ethyl α-aminobenzoylacetate, was dissolved in 20 c.c. of water, mixed with 5 g. of potassium thiocyanate in 10 c.c. of water, and heated in boiling water for 3 hours, when the thiol-ester separated; after crystallisation from alcohol, 4·8 g. were obtained in a pure state (40% of the theoretical yield, calculated on the *iso*nitroso-ester). The aqueous filtrate from the thiol-ester deposited some 2-thiol-4-phenylglyoxaline on concentration.

Ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate crystallises from alcohol in plates, m. p. 219° (corr.). It is insoluble in water, slightly soluble in cold alcohol, but readily soluble in chloroform or hot alcohol. (0·1291 gave 0·2742 CO_2 and 0·0587 H_2O. C = 57 H = 5·1. $C_{12}H_{12}O_2N_2S$ requires C = 58·1; H = 4·

and the chloroform residue mixed with a hot aqueous solution of
0·24 g. of picric acid, when 0·29 g. (yield 86%) of 4(5)-phenyl-
glyoxaline picrate separated; m. p. 212° (uncorr.) alone or mixed
with an authentic specimen.

We desire to thank the Council of the Lord Kitchener National
Memorial Fund for the grant of a scholarship which has enabled one
of us (W. G. F.) to take part in the investigation.

LXXXVI.—*The Relation of Pilocarpidine to Pilo-carpine. Synthesis of* 1 : 4- *and* 1 : 5-*Dimethylgly-oxalines.*

By RICHARD BURTLES, FRANK LEE PYMAN, and JAMES ROYLANCE.

HARNACK's suggestion (*Annalen*, 1887, **238**, 228) that pilocarpidine
is the imino-compound corresponding to pilocarpine is now proved
to be correct by its conversion by methylation into a mixture of
pilocarpine and an isomeric base, neo*pilocarpine* (I). Since pilo-
carpine is stereoisomeric with *iso*pilocarpine (Jowett, J., 1905,
87, 794) and the latter yields on distillation with soda-lime 1 : 5-
dimethylglyoxaline, and therefore contains the homopilopic com-
plex in the 5-position with respect to the 1-methyl group, it is
obvious that *neo*pilocarpine is the structural isomeride of pilocarpine

$$\text{C}_2\text{H}_5\text{·CH—CH·CH}_2\text{·C}\underset{\underset{\text{O}}{\diagdown\diagup}}{\overset{\begin{array}{c}\text{CH—NMe}\\ \end{array}}{\text{CO} \quad \text{CH}_2}}\text{—N}\!\!>\!\!\text{CH}$$

(I.)
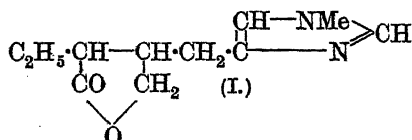
containing the homopilopic complex in the 4-position with respect
to the 1-methyl group. Like pilocarpine, *neo*pilocarpine is partially
racemised by alkali with the formation of a stereoisomeric base,
isoneo*pilocarpine*. Dr. J. H. Burn of the National Institute for
Medical Research kindly tested *neo*pilocarpine, and reports that it
has a very weak stimulating action on isolated intestinal muscle,
but no perceptible trace of true pilocarpine action. In an anæsthe-
tised cat, 100 mg., injected intravenously, caused a slight rise of
arterial blood pressure, with no trace of inhibition of the heart's
action, or of salivary secretion, whereas 0·1 mg. of pilocarpine, given
subsequently, produced both these effects in typical form.

The identity of the dimethylglyoxaline obtained by the degrada-

tion of isopilocarpine as the 1 : 5-isomeride was proved earlier (J., 1922, **121**, 2616) by an analytical method. The results have now been supplemented by the synthesis of this base (IV) by the oxidation of 2-*thiol*-1 : 5-*dimethylglyoxaline* (III), prepared in good yield by the condensation of α-*methylaminopropionacetal* (II) with thiocyanic acid—an obvious extension of the Wohl-Marckwald method to a secondary amino-acetal.

(II.) $(EtO)_2CH \cdot CHMe \cdot NHMe + HCNS \longrightarrow$

(III.) $\begin{matrix} CMe—NMe \\ \parallel \\ CH———N \end{matrix}\!\!\!>\!C \cdot SH \longrightarrow \begin{matrix} CMe—NMe \\ \parallel \\ CH———N \end{matrix}\!\!\!>\!CH$ (IV.)
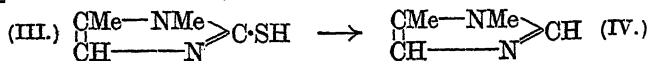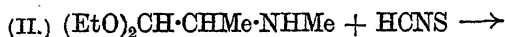
The isomeric 1 : 4-dimethylglyoxaline (XI) has also been synthesised by the oxidation of 2-*thiol*-1 : 4-*dimethylglyoxaline* (X), but the formation of the latter compound did not proceed so smoothly as was expected. Whereas Wohl and Marckwald (*Ber.*, 1889, **22**, 568, 1354; 1892, **25**, 2355) have shown that acetalyl alkyl (or aryl) thiocarbamides of the general formula $(OEt)_2CH \cdot CH_2 \cdot NH \cdot CS \cdot NHR$ readily yield on short hydrolysis with dilute mineral acids 2-thiol-1-alkyl (or aryl) glyoxalines, the condensation product of α-*amino-propionacetal* (V) and methylthiocarbimide—doubtless α-propion-acetalylmethylthiocarbamide (VI)—gave only 8% of 2-thiol-1 : 4-dimethylglyoxaline, the main product being a base, $C_7H_{14}ON_2S$, which is slowly converted into 2-thiol-1 : 4-dimethylglyoxaline on boiling with dilute mineral acids, but yields, besides this compound and its *S*-ethyl ether,[*] 2-methylamino-4-methylthiazole (XII) when heated at 150° with concentrated hydrochloric acid. The latter base was prepared for comparison by the action of chloroacetone upon methylthiocarbamide, a method previously employed by Traumann (*Annalen*, 1888, **249**, 31) and Young and Crookes (J., 1906, **89**, 59), neither of whom obtained it in a pure state.

Now towards hydrochloric acid at 150°, 2-thiol-1 : 4-dimethyl-glyoxaline is quite stable, and 2-methylamino-4-methylthiazole, although not recoverable wholly unchanged, is not converted into 2-thiol-1 : 4-dimethylglyoxaline. Both compounds therefore arise by the removal of a molecule of alcohol from the base $C_7H_{14}ON_2S$. Of the two formulæ VII and IX for this base, only the second represents a compound which would be expected to have more than feeble basic properties, and it thus appears that this substance is 2-*methylamino-5-ethoxy-4-methyl-4* : 5-*dihydrothiazole* (IX). With the adoption of this formula, the varying results of hydrolysis may be readily deduced from the knowledge that half-acetals are readily hydrolysed by hot dilute mineral acids, whereas the de-ethoxylation

* The ease of formation of this substance from the thiol compound is remarkable (compare p. 588).

of the ethoxy-derivatives of cyclic compounds requires the use of strong acids at high temperatures. Here strong hydrochloric acid at 150° converts the substance (partly) into XII, doubtless by way of the 5-hydroxy-4 : 5-dihydro-compound, whilst dilute mineral acids at lower temperatures are unable to effect the direct de-ethoxylation of (IX), but convert it into (X), presumably by fission of the nucleus and hydrolysis leading first to the half-acetal (VIII), and then to the corresponding aldehyde, which yields (X) by internal condensation.

$$(EtO)_2CH \cdot CHMe \cdot NH_2 + MeNCS \longrightarrow (EtO)_2CH \cdot CHMe \cdot NH \cdot CS \cdot NHMe$$
$$(V.) \qquad\qquad\qquad\qquad\qquad (VI.)$$

$$\begin{array}{c}CH(OEt) \cdot NMe \\ CHMe \rule{1cm}{0.4pt} N\end{array}\!\!\Big>C \cdot SH \quad \begin{array}{c}HO \cdot CH \cdot OEt \\ CHMe \rule{1cm}{0.4pt} N\end{array}\!\!\begin{array}{c}HS \cdot C \cdot NHMe\end{array} \rightleftharpoons \begin{array}{c}CH(OEt) \cdot S \\ CHMe \rule{1cm}{0.4pt} N\end{array}\!\!\Big>C \cdot NHMe$$
$$(VII.) \qquad\qquad\qquad (VIII.) \qquad\qquad\qquad (IX.)$$

$$\begin{array}{c}CH \cdot NMe \\ CMe \rule{1cm}{0.4pt} N\end{array}\!\!\Big>C \cdot SH \rightarrow \begin{array}{c}CH \cdot NMe \\ CMe \rule{1cm}{0.4pt} N\end{array}\!\!\Big>CH \qquad \begin{array}{c}CH \rule{0.6cm}{0.4pt} S \\ CMe \cdot N\end{array}\!\!\Big>C \cdot NHMe$$
$$(X.) \qquad\qquad\qquad (XI.) \qquad\qquad\qquad (XII.)$$
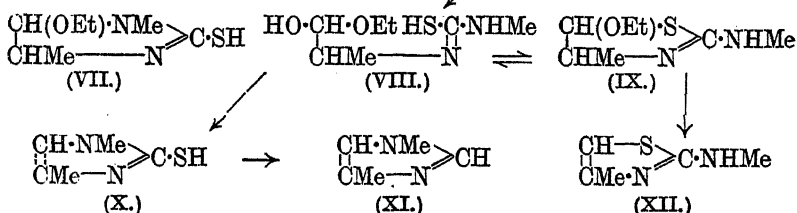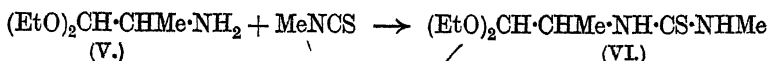
It was found that α-*propionacetalylphenylthiocarbamide* (XIII) gave on short hydrolysis with dilute mineral acids only 28% of 2-*thiol*-1-*phenyl*-4-*methylglyoxaline* (XIV), the main product of the reaction being a base, $C_{12}H_{16}ON_2S$, of similar character to the base $C_7H_{14}ON_2S$ and presumably therefore 2-*anilino*-5-*ethoxy*-4-*methyl*-4 : 5-*dihydrothiazole* (XV).

$$(EtO)_2CH \cdot CHMe \cdot NH \cdot CS \cdot NHPh \text{ (XIII.)} \longrightarrow$$

$$(XIV.) \begin{array}{c}CH \cdot NPh \\ CMe \rule{1cm}{0.4pt} N\end{array}\!\!\Big>C \cdot SH \quad \text{and} \quad \begin{array}{c}CH(OEt) \cdot S \\ CHMe \rule{1cm}{0.4pt} N\end{array}\!\!\Big>C \cdot NHPh \text{ (XV.)}$$
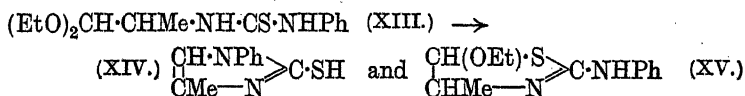
These facts led us to reinvestigate the behaviour of acetalyl-phenylthiocarbamide. Wohl and Marckwald found that whilst hot 30% sulphuric acid converted this substance into 2-thiol-1-phenylglyoxaline, cold concentrated sulphuric acid transformed it into a base, $C_{11}H_{16}O_2N_2S$, which gave a picrate and chloroplatinate derived from the anhydro-form, $C_{11}H_{14}ON_2S$, to which they attributed the formula XVI or XVII, since it gave 2-thiol-1-phenyl-

$$(XVI.) \begin{array}{c}CH(OEt) \cdot NPh \\ CH_2 \rule{1cm}{0.4pt} NH\end{array}\!\!\Big>CS \qquad \begin{array}{c}CH(OEt) \cdot NPh \\ CH_2 \rule{1cm}{0.4pt} N\end{array}\!\!\Big>C \cdot SH \text{ (XVII.)}$$
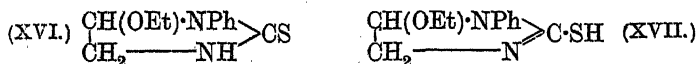
glyoxaline on hydrolysis with dilute sulphuric acid. We find that the free base has the formula $C_{11}H_{14}ON_2S$ as in the salts, that it is also formed to a slight extent, together with 2-thiol-1-phenyl-glyoxaline, on hydrolysis of the thiocarbamide with dilute sulphuric acid, and that it yields with hydrochloric acid at 150° not only

2-thiol- and 2-*ethylthiol*-1-*phenylglyoxalines*, but also a small pro-
portion of 2-anilinothiazole. It is clearly of similar character to
the base $C_7H_{14}ON_2S$ and would thus appear to be 2-anilino-5-
ethoxy-4 : 5-dihydrothiazole.   One other similar case is recorded
by Marckwald (*Ber.*, 1892, **25**, 2355), who states that acetalyl-*m*-
xylylthiocarbamide yields on treatment with strong sulphuric acid
a crystalline base, $C_{13}H_{20}O_2N_2S$, giving a picrate,

$$C_{13}H_{18}ON_2S,C_6H_3O_7N_3.$$
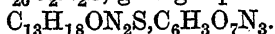
We repeated this experiment and obtained the picrate, but did not
obtain the base in a crystalline condition, either directly or through
the picrate.   We were therefore unable to determine its composi-
tion, but have no doubt that it is constituted similarly to the base
$C_7H_{14}ON_2S$, and that, if his analyses are correct, it contains a
molecule of water of crystallisation.

From these results, the conclusion is drawn that the primary
products of hydrolysis of acetalyl alkyl (or aryl) thiocarbamides
with aqueous mineral acids at 100° are half-acetals, and that these
form equilibrium mixtures with their anhydro-derivatives—the
5-ethoxy-4 : 5-dihydro-2-alkyl (or aryl)aminothiazoles—and water,
the condition of equilibrium being determined by the substituents
present.

Experimental.

Methylation of Pilocarpidine.—The base from 15 g. of pure pilo-
carpidine nitrate was mixed with 15 c.c. of methyl iodide.   Reaction
took place spontaneously, and was completed by heating for 1 hour
on the water-bath under reflux.   The bases were regenerated and
converted into nitrates.   On then adding ammonia and silver
nitrate, unchanged pilocarpidine was precipitated as the silver salt,
whilst chloroform extracted the tertiary bases from the filtrate.
They were converted into nitrates and crystallised from absolute
alcohol, when pilocarpine nitrate (1·8 g.) separated.   The bases
regenerated from the mother-liquors were converted into hydro-
chlorides, and the solution was evaporated to a syrup and mixed
with acetone, when *neo*pilocarpine hydrochloride (2·1 g.) separated.
Repetition of these operations gave a further 0·15 g. of each salt,
whilst the remaining mixture of tertiary bases amounted to only
0·4 g.   The crude pilocarpine nitrate melted at 173° and after
crystallisation from alcohol melted at 178° (corr.), alone or mixed
with an authentic specimen, and had $[\alpha]_D + 80°$ ($c = 3·9$ in water).
To confirm its identification the picrate was prepared; it melted
at 159—160° (corr.), alone or mixed with an authentic specimen.
Petit and Polonowski (*J. Pharm.*, 1897, **5**, 430) give its m. p. as
159—160°, Jowett (*J.*, 1900, **77**, 494) as 147°, but Dr. Jowett, who

kindly repeated its preparation—at the author's request—has since found the m. p. 161—162°.

neo*Pilocarpine hydrochloride* crystallises in large prisms on addition of acetone to its concentrated aqueous or alcoholic solution. It melts at 177° (corr.) and is deliquescent, and very easily soluble in water or alcohol. 0·1270 gave 0·2500 CO_2 and 0·0800 H_2O. C = 53·7; H = 7·1.   0·1696 gave 0·0994 AgCl.   Cl = 14·5. $C_{11}H_{16}O_2N_2$,HCl requires C = 54·0; H = 7·0; Cl = 14·5%. In aqueous solution (c = 4·116) it had $[\alpha]_D$ + 66·4°.

The *base* melts at 39—40° (corr.) and is readily soluble in water or organic solvents except light petroleum. The *nitrate* crystallises from absolute alcohol in rosettes of fine needles, m. p. 94—95° (corr.). It is not deliquescent, but is easily soluble in water or hot alcohol. The *picrate* crystallises from alcohol in fine needles, m. p. 117—119° (corr.).

isoneo*Pilocarpine* was prepared by boiling 0·7 g. of *neo*pilocarpine with 1 g. of potassium hydroxide in 1 c.c. of water and 10 c.c. of alcohol for 2 hours under reflux, and isolated as *picrate*, which formed yellow, prismatic needles, from alcohol, m. p. 125—126° (corr.). 0·1211 gave 0·2076 CO_2 and 0·0503 H_2O. C = 46·8 ; H = 4·7. $C_{11}H_{16}O_2N_2$,$C_6H_3O_7N_3$ requires C = 46·7; H = 4·3%. The *nitrate* crystallised from absolute alcohol in prisms, m. p. 105—106° (corr.), which were not deliquescent.   The hydrochloride was not obtained in crystalline form.

α-Bromopropionacetal was obtained as an oil (b. p. 74—75°/16—17 mm.) by Stoermer (*Annalen*, 1900, **312**, 271), following Kraus (*Diss.*, Berlin, 1895), in a yield of 36% of the theoretical by a method not described in detail but similar to that used for the preparation of bromoacetal (yield 31% of the theoretical) by Fischer and Landsteiner (*Ber.*, 1892, **25**, 2549).   By using dry ether as a diluent in the later stages of the bromination and eventually extracting the product completely with ether, the yield may be improved.   Under these conditions, propionacetal (100 g., b. p. 121—125°) and calcium carbonate (40 g.) treated with bromine (126 g.) below 5° gave α-bromopropionacetal (87·6 g., b. p. 69°/14 mm.   Yield 54%). (Found : Br = 37·7.   Calc., Br = 37·9%).

α-Aminopropionacetal (V).—The *dl*-form has not been described in accessible literature, although it seems to have been made by Kraus (*loc. cit.*); compare Wohl (*Ber.*, 1908, **41**, 3599).   Ammonia (56 g.) was passed into 95% alcohol (250 g.) at 0°, 31 g. of α-bromopropionacetal were added, and the mixture was heated for 12 hours at 125—130° in a steel autoclave.   After distilling off the alcohol and ammonia, adding a little water, and extracting with ether, potassium carbonate was added, and the mixture extracted with

chloroform. This extract gave on distillation 9·8 g. of α-amino-propionacetal, boiling at 79—80°/40 mm. (yield 46%). It is a colourless liquid miscible with water, alcohol or chloroform, but less soluble in ether. 0·1001 gave 0·2074 CO_2 and 0·1037 H_2O. C = 56·5; H = 11·6. 0·1621 gave, by Kjeldahl's method, 0·0192 NH_3. N = 9·8. $C_7H_{17}O_2N$ requires C = 57·1; H = 11·6; N = 9·5%.

α-*Methylaminopropionacetal* (II) was prepared similarly from the product obtained by heating anhydrous methylamine (47 g.) in absolute alcohol (45 g.) with α-bromopropionacetal (47 g.) for 10 hours at 125—130°, when 18 g. (yield 50%) were obtained as a colourless oil, b. p. 66—69°/16—18 mm., and having similar solubilities to the previous compound. 0·0974 gave 0·2111 CO_2 and 0·1013 H_2O. C = 59·6; H = 11·6. 0·0742 gave by Kjeldahl's method, 0·0078 NH_3. N = 8·7. $C_8H_{19}O_2N$ requires C = 59·6; H = 11·8; N = 8·7%. Poorer yields of this compound were obtained by decreasing the time of reaction, the concentration of methylamine or its quantity relative to that of the acetal, or by increasing the temperature.

Condensation with Thiocyanic Acid.—α-Methylaminopropionacetal (2 g.) was added to a mixture of potassium thiocyanate (1·3 g. in 6 c.c. of water) and hydrochloric acid (1·2 c.c of conc. acid). After heating for 1 hour on the water-bath, another 0·5 c.c. of hydrochloric acid was added, and the liquid was concentrated on the water-bath, when 2-thiol-1 : 5-dimethylglyoxaline separated (1·45 g., pure, yield 91%). After adding sodium hydroxide to the mother-liquor, nothing was extracted by ether.

2-*Thiol*-1 : 5-*dimethylglyoxaline* (III) crystallises from water in colourless prisms, m. p. 261—262° (corr.) to a deep red liquid. It is very sparingly soluble in cold water, but readily soluble in boiling water, sparingly soluble in cold alcohol, and insoluble in ether. It dissolves readily in aqueous sodium hydroxide, and slowly in 5N-hydrochloric acid, but is insoluble in aqueous sodium carbonate or ammonia. 0·1025 gave 0·1754 CO_2 and 0·0579 H_2O. C = 46·7; H = 6·3. 0·1378 gave, by Kjeldahl's method, 0·0357 NH_3. N = 21·3. 0·1497 gave 0·2770 $BaSO_4$. S = 25·4. $C_5H_8N_2S$ requires C = 46·9; H = 6·3; N = 21·9; S = 25·0%. On oxid-ation with hot 10% nitric acid it gave 1 : 5-dimethylglyoxaline (yield 67%), which was isolated as picrate, m. p. 167—168° (corr.) alone or mixed with an authentic specimen, and further identified as chloroaurate, decomp. 218—219° (corr.) (Found : Au = 45·2. Calc., Au = 45·0%).

Condensation of α-*Aminopropionacetal with Methylthiocarbimide.* —A. α-Aminopropionacetal (7·7 g.) and methylthiocarbimide (3·9 g.) were mixed, when heat was developed. The product, which did

not crystallise on keeping over-night, was boiled with 20 c.c. of $5N$-hydrochloric acid for 20 minutes under reflux. The solution was evaporated to a syrup, mixed with an excess of sodium hydroxide, and extracted with ether, which removed 8·5 g. of yellow oil. The alkaline mother-liquor deposited on acidification 2-thiol-1 : 4-dimethylglyoxaline (0·51 g., m. p. 209°), and after concentration a further 0·05 g., m. p. 204° (yield 8·4%). The yellow oil was added to 11 g. of picric acid in 100 c.c. of hot alcohol, when 15·0 g. of 2-methylamino-5-ethoxy-4-methyl-4 : 5-dihydrothiazole picrate, m. p. 157—158°, separated on cooling (yield 71%).

B. The condensation product of α-aminopropionacetal and methylthiocarbimide gave, after boiling under reflux for 6 and 16 hours, respectively, with hydrochloric acid (5 c.c. of $5N$-acid per g.), 2-thiol-1 : 4-dimethylglyoxaline (pure, yields 40 and 32%), 2 - methylamino - 5 - ethoxy - 4 - methyl-4 : 5 - dihydrothiazole (yields of pure picrate 14 and 2%), and 2-ethylthiol-1 : 4-dimethylglyoxaline (yields of picrate, m. p. *ca.* 101°, 18 and 40%).

2-*Thiol*-1 : 4-*dimethylglyoxaline* (X) crystallises from water in colourless, elongated prisms, m. p. 211—212° (corr.) to a deep red liquid. It is sparingly soluble in cold water, readily soluble in $5N$-hydrochloric acid or aqueous sodium hydroxide, but insoluble in aqueous sodium carbonate or ammonia. It is sparingly soluble in alcohol and very sparingly soluble in ether. 0·1022 gave 0·1752 CO_2 and 0·0602 H_2O. C = 46·8; H = 6·6. $C_5H_8N_2S$ requires C = 46·9; H = 6·3%. It was recovered unchanged after being heated with hydrochloric acid (5 c.c. of conc. acid to 1 g.) for 3 hours at 150°. On oxidation with hot dilute nitric acid, it gave 1 : 4-dimethylglyoxaline (yield 50%), which was isolated and identified as the picrate, which melted, alone or mixed with an authentic specimen, at 167—168° (corr.).

2-*Methylamino-5-ethoxy-4-methyl-4* : 5-*dihydrothiazole* (IX) was recovered from the picrate, through the hydrochloride, as a colourless oil, which solidified slowly and then melted at 52° (corr.). 0·0868 gave 0·1524 CO_2 and 0·0642 H_2O. C = 47·9; H = 8·3. $C_7H_{14}ON_2S$ requires C = 48·3; H = 8·0%. It is insoluble in water, but very easily soluble in the usual organic solvents except light petroleum. The hydrochloride, hydriodide, and nitrate were not obtained in crystalline form. The *picrate* crystallised from alcohol in yellow needles, m. p. 158° (corr.). 0·1253 gave 0·1768 CO_2 and 0·0508 H_2O. C = 38·5; H = 4·5. 0·1705 gave 0·1013 $BaSO_4$. S = 8·2. $C_7H_{14}ON_2S,C_6H_3O_7N_3$ requires C = 38·7; H = 4·2; S = 7·9%. The *chloroplatinate* crystallised in yellow-brown scales, m. p. 201° (corr.; decomp.) on mixing cold concentrated solutions of platinic chloride and the hydrochloride. It was

decomposed by heating its aqueous solution and was therefore not recrystallised. 0·1470 gave 0·0372 Pt. Pt = 25·3.

$$(C_7H_{14}ON_2S)_2,H_2PtCl_6$$
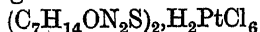
requires Pt = 25·7%.

Hydrolysis of IX.—*A.* 2·0 Grams were boiled with 30% sulphuric acid (10 c.c.) for ½ hour, and mixed with sodium hydroxide, when 1·4 g. were removed (unchanged) by ether. On acidifying the alkaline liquor and concentrating, crude 2-thiol-1 : 4-dimethylglyoxaline (0·15 g., m. p. 195°, yield 10%) separated, and gave the pure substance (m. p. 212° alone or mixed) after crystallisation from dilute hydrochloric acid.

B. The hydrochloride (from 7·0 g. of picrate), boiled with 37 c.c. of 5N-hydrochloric acid for 6 hours, gave 2-thiol-1 : 4-dimethylglyoxaline (1·32 g., m. p. 212°, yield 59%) and 0·6 g. of very crude ethoxy-base, which gave impure picrate (0·75 g., m. p. 145—148°, not depressed by admixture with the picrate, m. p. 157—158°).

C. Ten grams and 50 c.c. of concentrated hydrochloric acid were heated for 3 hours at 150°. After evaporation, the residue was crystallised from absolute alcohol (mother-liquor L) and gave 2·4 g. (m. p. 226°). After crystallisation from absolute alcohol, it melted at 228° (corr.) and was found by the mixed-melting-point method and analysis to be identical with 2-*methylamino*-4-*methyl-thiazole hydrochloride* (yield 25%) described below (0·1038, dried at 120°, gave 0·1384 CO_2 and 0·0548 H_2O. C = 36·4; H = 5·9. 0·2034, dried at 120°, gave 0·1770 AgCl. Cl = 21·5. $C_5H_8N_2S,HCl$ requires C = 36·5; H = 5·5; Cl = 21·5%). Identification was confirmed by comparison of the base, hydriodide, and chloroplatinate from each source.

The mother-liquor L was basified with sodium hydroxide, extracted with ether, faintly acidified, and concentrated, when 2-thiol-1 : 4-dimethylglyoxaline (0·15 g. ; m. p. 212°, alone or mixed ; yield 2%) separated. The ether left an oil, which gave 2-*ethylthiol-1 : 4-dimethylglyoxaline picrate* (5·35 g. ; m. p. *ca.* 103° ; yield 24%). It separates from alcohol in quadrilateral tablets, m. p. 105° (corr.). 0·1016 gave 0·1514 CO_2 and 0·0374 H_2O. C = 40·6; H = 4·1. 0·0818 gave 12·8 c.c. moist N_2 (19·5°, 772 mm.). N = 18·2. $C_7H_{12}N_2S,C_6H_3O_7N_3$ requires C = 40·5; H = 3·9; N = 18·2%. The same salt was obtained from (a) the product of interaction of 2-thiol-1 : 4-dimethylglyoxaline and ethyl iodide at 100°, and (b) the product of boiling 2-thiol-1 : 4-dimethylglyoxaline (1 g.) with 5N-hydrochloric acid (20 c.c.) and alcohol (2 c.c.) for 20 hours under reflux (yield 58%).

The *hydrochloride* crystallises from acetone in deliquescent plates, m. p. 125—127° (corr.).

2-*Methylamino*-4-*methylthiazole* (XII) was prepared after Trau-
mann (*Annalen*, 1888, **249**, 31) by gently warming a mixture of
chloroacetone (12·4 g.) and methylthiocarbamide (12·2 g.), mixing
the product with sodium hydroxide, and extracting the base with
ether, when a sparingly soluble, basic by-product (2·1 g., m. p.
211° decomp.) separated. The oil left on removing the ether was
mixed with absolute alcohol and acidified with gaseous hydrogen
chloride, when, on keeping, 6·7 g. of the hydrochloride (m. p. 225°)
separated. It crystallised from absolute alcohol in prismatic
needles, m. p. 228° (corr.), which were very easily soluble in water.
From a strong aqueous solution, sodium hydroxide precipitated
the base, which crystallised from alcohol in prisms, m. p. 71·5—72·5°
(corr.) (Found : C = 46·8 ; H = 6·6. Calc., C = 46·8 ; H = 6·3%).
Traumann describes it incorrectly as hygroscopic and gives the m. p.
42° ; Young and Crookes (J., 1906, **89**, 59) give m. p. 64°. The
hydriodide, fine needles from water, had m. p. 194° (decomp. ;
corr.) (Traumann, 136°), whilst the chloroplatinate, serrated, pris-
matic needles, had m. p. 180° (decomp. ; corr.) (Traumann, 167°).
The base gave with methyl iodide 2-methylamino-3 : 4-dimethyl-
thiazole hydriodide, m. p. 165—166° (corr.) (Young and Crookes,
164°). 2-Methylamino-4-methylthiazole hydrochloride is not com-
pletely stable towards hydrochloric acid (5 c.c. to 1 g.) at 150°
(3 hours), for only 30% was recovered unchanged in a pure state,
but the remainder (of lower m. p.) did not contain 2-thiol-1 : 4-
dimethylglyoxaline.

α-*Propionacetalylphenylthiocarbamide* (XIII) was obtained by
mixing α-aminopropionacetal (6·8 g.) with phenylthiocarbimide
(6·3 g.) and crystallising the product from alcohol (yield 71%).
It formed needles from alcohol, m. p. 110° (corr.). 0·1066 gave
0·2338 CO_2 and 0·0720 H_2O. C = 59·8 ; H = 7·6. $C_{14}H_{22}O_2N_2S$
requires C = 59·5 ; H = 7·9%.

Hydrolysis.—7·5 Grams of the above compound were boiled with
20 c.c. of 5N-hydrochloric acid for ½ hour under reflux. On con-
centration, 1·2 g. of 2-thiol-1-phenyl-4-methylglyoxaline separated,
and on then working up the mother-liquor as on p. 587 a further
0·2 g. of the thiol compound (total yield 28%) and 7·9 g. of 2-*anilino*-
5-*ethoxy*-4-*methyl*-4 : 5-*dihydrothiazole picrate* (XV) (yield 64%)
were obtained. This salt separates from alcohol, in which it is
sparingly soluble in the cold, in yellow needles, m. p. 163—165°
(corr.). 0·1010 gave 0·1728 CO_2 and 0·0406 H_2O. C = 46·7 ;
H = 4·5. $C_{12}H_{16}ON_2S,C_6H_3O_7N_3$ requires C = 46·4 ; H = 4·1%.

2-*Thiol*-1-*phenyl*-4-*methylglyoxaline* (XIV) crystallised from alcohol
in well-formed, colourless prisms, m. p. 190—191° (corr.). It is
very sparingly soluble in hot water, but soluble in aqueous sodium

hydroxide. 0·1010 gave 0·2328 CO_2 and 0·0508 H_2O.   C = 62·9;
H = 5·6. $C_{10}H_{10}N_2S$ requires C = 63·1; H = 5·3%.

Acetalylphenylthiocarbamide (2·0 g.) [prepared after Wohl and
Marckwald in 80% yield, large prisms from alcohol, m. p. 96°
(corr.)], boiled with 5N-hydrochloric acid (10 c.c.) for ½ hour, gave,
on cooling, pure 2-thiol-1-phenylglyoxaline [1·02 g., m. p. 181—182°
(corr.), yield 78%]; after addition of sodium hydroxide, ether
collected 0·2 g. of base yielding a picrate (0·25 g.), m. p. 196° alone or
mixed with the picrate of the ethoxy-base described below. When
the hydrochloric acid was replaced by 30% sulphuric acid (10 c.c.),
the yield of the thiol compound was the same, but the recovered
ethoxy-base was less pure.

2 - Anilino - 5 - ethoxy-4 : 5 - *dihydrothiazole.* — Acetalylphenylthio-
carbamide (12 g.) was stirred into concentrated sulphuric acid
(30 c.c.) below 0°.   After ½ hour, the solution was poured on to ice,
and mixed with sodium hydroxide; ether then extracted the ethoxy-
base (10 g., almost pure). It crystallises from moist alcohol in
prismatic needles, m. p. 92—93° (corr.).   0·1060 gave 0·2316 CO_2
and 0·0638 H_2O.   C = 59·6; H = 6·7.   0·2486 in 16·62 benzene
(cryoscopic) gave Δ 0·31°, M = 236. $C_{11}H_{14}ON_2S$ requires
C = 59·4; H = 6·3%; M = 222).   Wohl and Marckwald give
m. p. 94° and composition $C_{11}H_{16}O_2N_2S$.   The picrate melted at
198° (corr.); W. and M. give dec. 190°.

Hydrolysis.—A. The ethoxy-base (3 g.) was boiled with 30%
sulphuric acid (15 c.c.) for ½ hour, mixed with water (15 c.c.), and
cooled.   The solution deposited 2-thiol-1-phenylglyoxaline (2·0 g.,
m. p. 175°, yield 84%), from which the pure substance (1·75 g.)
was obtained by crystallisation from water. The mother-liquors,
mixed with sodium hydroxide, and extracted with ether, gave
0·25 g. of crude ethoxy-base (semi-crystalline; it gave a picrate, m. p.
185°, which did not depress the m. p. of the ethoxy-base picrate).

B. The ethoxy-base (2 g.) was heated with concentrated hydro-
chloric acid (10 c.c.) for 3 hours at 150°.   On concentrating and
adding water, 2-thiol-1-phenylglyoxaline (0·27 g., m. p. 181—182°,
yield 17%) separated.   After the filtrate had been mixed with
sodium hydroxide, ether collected an oil (1·3 g.), which was mixed
with picric acid (1·5 g.) in hot alcohol (45 c.c.), when 2-anilino-
thiazole picrate (0·12 g., m. p. 198—199°, yield 3·3%) separated from
the hot solution, followed, on cooling, by 2-*ethylthiol-1-phenyl-
glyoxaline picrate* (2·4 g., m. p. 117—118°, yield 61%). It separated
from alcohol in yellow needles, m. p. 119—120° (corr.).   0·1044
gave 0·1798 CO_2 and 0·0338 H_2O.   C = 47·0; H = 3·6.   0·0776
gave 10·7 c.c. moist N_2 at 16·5° and 772 mm.   N = 16·4.
$C_{11}H_{12}N_2S,C_6H_3O_7N_3$ requires C = 47·1; H = 3·5; N = 16·2%.

The same salt was obtained readily from the products of inter-action of 2-thiol-1-phenylglyoxaline with (a) ethyl iodide at 100°, (b) hydrochloric acid (5 c.c. of conc. acid to 1 g.) and alcohol (1 c.c.) at 150°.

The base formed an oil, b. p. 310°/772 mm. with slight decomposition. 0·1090 gave 0·2578 CO_2 and 0·0592 H_2O. C = 64·5; H = 6·1. $C_{11}H_{12}N_2S$ requires C = 64·7; H = 5·9%. 2-Thiol-1-phenyl-glyoxaline melts at 181—182° (corr.) (W. and M., 181°). After heating it (1 g.) with concentrated hydrochloric acid (5 c.c.) for 3 hours at 150°, 0·9 g. was recovered unchanged. The 2-anilinothiazole was identified by comparison of the base and picrate with the substance obtained by Traumann's method (loc. cit.) (yield 66%) and its picrate. The bases and a mixture melted at 127—128° (corr.); Traumann gives 126°; Näf (Annalen, 1891, 265, 108) gives 124°. The picrate from each source and a mixture had m. p. 198—199° (corr.); this salt is very sparingly soluble in hot alcohol. 2-Anilinothiazole can be recovered quantitatively unchanged after heating with hydrochloric acid (5 c.c. of. conc. acid to 1 g.) for 3 hours at 150°.

Acetalyl-m-xylylthiocarbamide, prepared from aminoacetal (2·78 g.) and m-xylylthiocarbimide (3·3 g.), was added to concentrated sulphuric acid (17 g.) at 0°. After an hour, the liquid was diluted with ice, extracted with ether, which removed 0·2 g. of oil, made alkaline with ammonia, and again extracted with ether, when an oil (4·5 g.) was obtained which did not crystallise on keeping. It was converted into picrate and crystallised fractionally from hot alcohol, when 1·0 g. of the salt described by Marckwald was obtained, having m. p. 142—143° (corr.) (Found : C = 47·4; H = 4·6. Calc., C = 47·6; H = 4·4%). The base regenerated from the pure salt did not crystallise.

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LXXXVII.—An X-Ray Investigation of Saturated Aliphatic Ketones.

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THIS paper is a continuation of the work on X-ray measurement of the higher members of the fatty acid series and their esters (Müller, J., 1923, 123, 2043; Shearer, ibid., p. 3152; Müller and Shearer, ibid., p. 3156) and deals in particular with saturated aliphatic ketones. By an examination of these compounds it was

hoped that confirmation of the suggestions put forward in the
previous papers would be obtained and that light would be thrown
on the effect on the molecular structure of a variation of the position
of the carbonyl group in the ketone molecule.

(1) *Preparation of Ketones.*—The ketones were prepared from the
corresponding normal fatty acids by the valuable catalytic method
of Senderens (*Compt. rend.*, 1909, **149**, 993); the apparatus used
was a modification of that of Pickard and Kenyon (J., 1911, **99**, 56).
Five gram-molecules of the more volatile acid were used to one of the
higher acid, this proportion yielding convenient amounts of the
mixed ketones, which were readily separated from those of higher
symmetry by vacuum distillation. The various products were

FIG. 1.

Total number of carbon atoms.
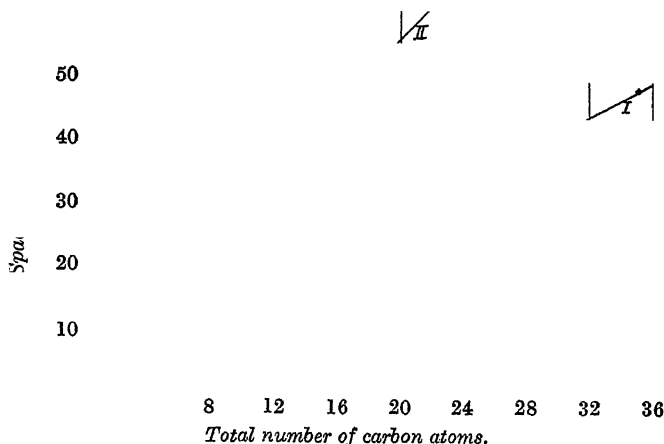
further purified by crystallisation from suitable solvents. It is
essential that the initial acids should be free from homologous
impurities, as otherwise the ketones cannot be obtained in a pure
state.

(2) *Experimental Procedure and Results.*—As in previous experi-
ments, a glass plate carrying a thin layer of the substance was
oscillated in an X-ray beam (FeKα radiation) and the spectra were
received on photographic plates. These spectra consist of a large
number of lines the majority of which are successive orders of
reflection from one plane in the crystal. This plane has a very much
larger spacing than any of the others and its spacing has been shown
to bear a close relation to the length of the molecule of the substance
under investigation. In a previous paper, arguments were advanced
to show that this spacing is probably, within narrow limits, a measure
of the length of a single molecule or of two molecules end to end.

It was also suggested that when the molecules contained at one end a chemically active group there was a tendency for the molecules to arrange themselves in pairs, whereas if there was no such active group at the end, no such tendency existed and the X-ray spacing measured was a measure of the length not of two, but of a single molecule. The following table gives a summary of the results of the measurements of the principal spacing.

Ketone.	Formula.	M. p.[1]	Spacing.
Di-n-hexyl	$C_6H_{13}\cdot CO\cdot C_6H_{13}$	30°	18·7
Methyl n-tridecyl	$CH_3\cdot CO\cdot C_{13}H_{27}$	39·5	42·4
Methyl n-pentadecyl	$CH_3\cdot CO\cdot C_{15}H_{31}$	48—48·5	47·6
Methyl n-hexadecyl	$CH_3\cdot CO\cdot C_{16}H_{33}$	52	50·0
Ethyl n-pentadecyl	$C_2H_5\cdot CO\cdot C_{15}H_{31}$	52·5	25·2
Hexyl n-undecyl	$C_6H_{13}\cdot CO\cdot C_{11}H_{23}$	45 *	25·2
Methyl n-heptadecyl	$CH_3\cdot CO\cdot C_{17}H_{35}$	55·5—56	52·9
Propyl n-pentadecyl	$C_3H_7\cdot CO\cdot C_{15}H_{31}$	50	26·3
Ethyl n-heptadecyl	$C_2H_5\cdot CO\cdot C_{17}H_{35}$	59·5—60	27·3
Propyl n-heptadecyl	$C_3H_7\cdot CO\cdot C_{17}H_{35}$	56 *	28·9
Hexyl n-pentadecyl	$C_6H_{13}\cdot CO\cdot C_{15}H_{31}$	54	31·1
Di-n-undecyl	$C_{11}H_{23}\cdot CO\cdot C_{11}H_{23}$	69·5	31·6
Hexyl n-heptadecyl	$C_6H_{13}\cdot CO\cdot C_{17}H_{35}$	62 *	33·6 (30·8)[2]
Di-n-tridecyl	$C_{13}H_{27}\cdot CO\cdot C_{13}H_{27}$	69·5	37·0
Di-n-pentadecyl	$C_{15}H_{31}\cdot CO\cdot C_{15}H_{31}$	76—76·5	41·1
Di-n-heptadecyl	$C_{17}H_{35}\cdot CO\cdot C_{17}H_{35}$	82·5	47·2

[1] Melting points were determined by the capillary-tube method. The values marked * have not been previously recorded.

[2] In addition to the 33·6 spacing a few orders of a spacing 30·8 also occur in the spectrum. These are probably due to a second crystalline modification (see Müller's paper on the hydrocarbons).

(3) *Interpretation of X-Ray Results.*—In Fig. 1 the results are shown graphically, the spacing being plotted against the total number of carbon atoms in the molecule. It will be observed that the ketones group themselves into two sets represented by the straight lines I and II. In either of these sets the continued addition of CH_2 groups to the molecule results in a uniform rate of growth of the spacing, thus confirming the result, previously deduced from the measurements of other series, that the size of this spacing bears a close relation to the length of the molecule. The actual values of the spacings in group I are what we should expect if only a single molecule existed between successive reflecting planes. In group II the spacing suggests a length double that of a single molecule. The condition previously suggested for the existence of a spacing corresponding to the length of a double molecule was that the molecule should possess an active group at its end. The end group of the ketone molecule is CH_3 if the formula be written
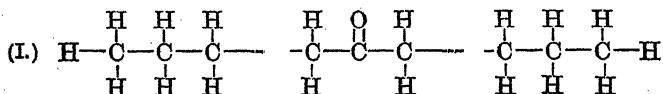
which, as we shall see later, is the most probable arrangement. Such an end group must be regarded as inactive chemically, and therefore, in accordance with our empirical rule, we should expect to find only one molecule between successive planes. Four of the ketones examined give, however, a spacing corresponding to two molecules. These four are not distributed at random, but are all methyl ketones in which there is only one CH_3 group separating the carbonyl group from the end of the molecule. It would appear, therefore, that in these cases the CO group is sufficiently near the end of the molecule for these methyl ketones to be considered as possessing an active end group—$CO \cdot CH_3$. In the ethyl, propyl, etc., ketones, the carbonyl group is too far from the end of the molecule to make its effect felt in the building of the crystal. If this inter-pretation is correct, it would appear to open up a method for the investigation of the range of action of the oxygen atom.

Further confirmation of this interpretation of the X-ray data as closely representing the lengths either of one or of two molecules comes from Fig. 1. If the spacings of the methyl ketones are halved, the points representing them fall, within the limits of experimental error, on the line representing the other members of the series. They are shown in the figure by circles. Typical photographs of groups I and II are shown in the first two spectra of Fig. 3. The first represents methyl heptadecyl ketone, the second propyl pentadecyl ketone. Both contain 19 carbon atoms, but it is clear that the spacing of the methyl ketone is twice that of the other, as is shown by the fact that the 2nd, 4th, 6th, 8th, etc., orders of the methyl ketone coincide with the 1st, 2nd, 3rd, 4th, etc., orders of propyl pentadecyl ketone. This would suggest that, when the spacing corresponds to the length of two molecules, these are so arranged in the crystal that there is little or no overlapping lengthwise of the two molecules. Further, it will be observed that the intercepts on the vertical axis of the lines I and II are approxim-ately 2 and 4 Å.U. This is just what we should expect from the extra hydrogens on the final carbons; in the case of a single molecule these would contribute about 2 Å.U., in the case of a double molecule 4 Å.U., to the spacing.

One of the chief reasons for the examination of the ketone series was the hope of discovering in this way the effect on the molecule of the position of the carbonyl group. The results show that this group has little, if any, effect on the length of the molecule as indicated by the X-ray spacing. The mere fact that all the points representing the ketones, after allowing for the double spacing in the methyl group, lie on the straight line in Fig. 1 indicates that the existence of the CO group in varying positions from near the end to

the centre of the molecule has little influence on the length of the molecule. That length appears to be a function of the total number of carbon atoms alone, and the CO group behaves for all practical purposes, as far as the length of the molecule is concerned, in the same way as if it were a CH_2 group. This also enables us to decide whether the graphic formula for a ketone should be written

$$\begin{matrix} C_nH_{2n+1} \\ C_mH_{2m+1} \end{matrix} > CO \quad \text{or} \quad C_nH_{2n+1} \cdot CO \cdot C_mH_{2m+1},$$
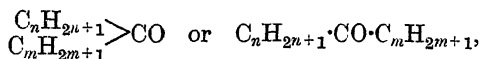
both of which formulæ are in common use at present. Consider the former formula. If the molecule really conformed to such an arrangement, the length would be determined by the length of a chain of $n + 1$ or $m + 1$ carbon atoms according as n is greater or less than m. In the case of the latter formula the length would be determined by a number, $n + m + 1$, of carbon atoms. Fig. 1 shows immediately that concordant results are obtained when $n + m + 1$ is plotted against the spacing, whereas if $n + 1$ or $m + 1$ were used chaos would result. Again, if the former were the true formula, we should expect such substances as ethyl or propyl heptadecyl ketone to show the same spacing as di-n-hepta-decyl ketone, whereas the table shows that they are very different. It must, however, be remembered that in the former case the position of the CO group at the end of the molecule would probably result in a crystal combination in which the spacing measured would correspond to twice the length of the molecule. If this were so, then the spacing would be determined by $2n + 2$ or $2m + 2$ according as n or m is the greater. This again is inconsistent with the observed results. We conclude, therefore, that the formula which is consistent with the X-ray data is the latter, and these results seem to indicate definitely that, in the solid state, the molecule has approximately this structure.

In a previous paper, certain arguments were advanced in support of the assumption that the angle between successive carbon atoms in the chain is the tetrahedral angle of 109° 28′. It was shown that there are three principal types of chain and that the observed rates of increase of length per CH_2 group are consistent with the assumption that the molecules are placed very nearly perpendicular to the principal reflecting planes and the carbon atoms are linked together in one or other of two of these types of chains. From Fig. 1 the average increase of the ketone spacing per CH_2 group is 1·30 Å.U., a value somewhat higher than the larger of the two increments previously found. Although the difference is small, it appears to be outside the experimental error, and it would seem that certain modifications of the suggestions put forward in previous papers may

be necessary. It is proposed shortly to publish a discussion of all the results so far obtained and the bearing of these results on the structure of the carbon chain. If the carbon atom has the same diameter as in diamond, the largest possible increase per carbon atom in a chain subject to the tetrahedral angle condition is 1·26, a value only just smaller than that observed.

Some doubt has been expressed (e.g., Wyckoff, "The Structure of Crystals," p. 379 et seq.) as to whether these substances are truly crystalline. It has been suggested that they are in an intermediate state between the solid and the liquid condition. If, for example, the molecules tended to orient themselves perpendicular to the glass surface, it is conceivable that we might get a series of successive layers of equal thickness in which the molecules were all arranged parallel to each other lengthwise. This would give a periodicity parallel to the length of the molecule, but no periodicity in any other direction. The result would be that the X-ray spectra would show only reflections from one plane. Whilst the majority of the lines on the plates are successive reflections from such a plane, other lines occur all of which correspond to relatively small spacings; these are not high orders of the main spacing, but are of independent origin, and a "Faser-diagram" photograph made from a small flake shows definitely that they originate in other planes in the crystal. In fact the behaviour of these substances is exactly like that of the ordinary crystal. Owing to their flaky nature, it is particularly easy to obtain reflections from the large-spacing plane, as the process of pressing the substances on to a glass plate tends to produce a special orientation in which these planes are set parallel to the surface of the glass, just as would happen if graphite were treated in the same way. There seems no reason for assuming that these substances differ in any material way from ordinary crystalline matter.

It has been pointed out that there is a difference between the methyl ketones and the others in that the spacing observed for the methyl ketones corresponds to that of planes separated by two molecules and not by a single molecule. It might be expected that this difference would make itself shown in other physical and in chemical ways. The most natural constant to examine is the melting point. The melting point is a function of the energy required to break down the crystalline structure, and it might well be expected that the binding of the methyl ketone molecules in the crystal would be stronger than that of those ketones which show only one molecule between successive planes and in which the CO group is further removed from the end of the molecule. An examination shows that the melting points of the methyl members of a series are

Fig. 3.
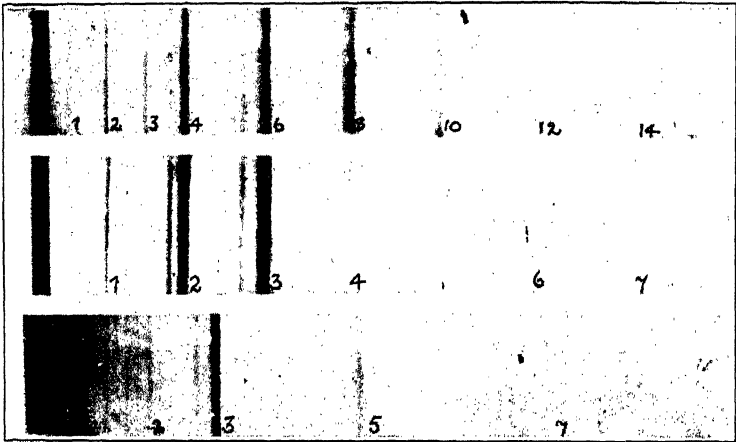
higher than would be expected from an extrapolation from the higher members of the series. It must be remarked, however, that the ethyl ketones also show high melting points, a result which the X-ray measurements would hardly anticipate. Perhaps some such property as this is of fairly common occurrence and may form the basis of an explanation of the fact that the first member of a series often differs in properties from the higher members.

A study of the distribution of intensity among the various orders of reflection from the principal plane leads to results which confirm the structure suggested above. It has been pointed out that the position of the carbonyl group does not affect the length of the molecule; it has, however, a very marked influence on the intensity distribution. On certain simple assumptions it is possible to calculate what the intensity distribution should be if the molecule conforms to the proposed structure. The carbon chain may be regarded

FIG. 2.
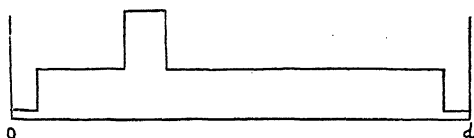
as a uniform distribution of scattering matter extending over the greater part of the distance between two planes; at the ends where the extra hydrogens occur there will be an almost complete absence of scattering matter, while there will be an excess at that point of the chain where the oxygen atom is situated. Fig. 2 represents diagrammatically such a structure. It is not proposed to enter into a mathematical analysis of the problem, as a full account of the method will be published elsewhere, but the results to be expected may briefly be indicated. If the oxygen occurs at the middle of the chain, as in the di-n-ketones, the odd orders will be strong and the even orders weak; if the oxygen is one-third of the way along the molecule, the third, sixth, ninth, etc., orders will tend to disappear; if one-quarter along, the fourth, eighth, etc., orders will be weak, and so on. Half-way between successive minima, positions of maximum intensity will occur. Such predictions are in complete agreement with observation. In Fig. 3, in the third photograph, which represents a di-n-ketone, the 1st, 3rd, and 5th orders are well marked, while the even orders are almost nonexistent. The second photograph represents propyl pentadecyl ketone, where the oxygen atom is about one-fifth of the way along; the higher orders do not show well in the reproduction, but there is a minimum at the fifth order with a corresponding maximum

between the second and third orders. The case of the di-n-ketones is of peculiar interest, as the intensity distribution shown by these compounds is found in many other series, *e.g.*, the fatty acids. In all the other cases where such a distribution has so far been observed, the X-ray spacing corresponds not to the length of a single molecule, but to that of two molecules. In a previous paper it was suggested that when two molecules existed lengthwise between two successive planes they were oriented in opposite directions. In the case of these ketones, we have to deal only with a single molecule, but it is clear that a molecule whose formula is $C_nH_{2n+1} \cdot CO \cdot C_nH_{2n+1}$ may be regarded as equivalent from this point of view to two half-molecules, $C_nH_{2n+1} \cdot (\frac{1}{2}CO)$, placed end to end in opposite directions. The fact that we find the same intensity distribution in the di-n-ketones and in the fatty acid series appears to be new evidence in favour of the suggestion that the two acid molecules which occur end to end between successive planes have their carboxyl groups oriented in opposite directions. Provided that the oxygen atom is kept at the same fractional distance from the end of the molecule, the intensity distribution is almost independent of the number of carbon atoms in the chain, just as, in cases where the chain is continuous, we find that the intensity distribution remains practically unaltered, although the number of carbons is varied within wide limits.

We see, therefore, that from a study of the X-ray spacing it is possible to determine the number of carbon atoms in the ketones, whilst a consideration of the intensity distribution enables us to locate, within reasonably narrow limits, the position of the carbonyl group.

LXXXVIII.—*Further X-Ray Measurements on Long-chain Compounds* (n-*Hydrocarbons*).

By ALEX MÜLLER and WILLIAM BRISTOW SAVILLE.

EXTENDING the work on X-ray investigations of long-chain compounds (Müller, J., 1923, **123**, 2043; Shearer, *ibid.*, p. 3152; Müller and Shearer, *ibid.*, p. 3156), this paper deals with new measurements made on normal hydrocarbons. The substances which had been investigated previously all contained at least one oxygen atom per molecule. It has now been shown that the absence of the oxygen atom has no appreciable influence on the reflecting power for X-rays, and this leads to the conclusion that the chain itself plays a predominant part in the reflection phenomena.

The technique was exactly the same as in the previous work. The substance was spread in a thin layer on a small strip of glass. The strip was then mounted on the table of an X-ray spectrometer and the spectra were photographed by exposing the substance to homogeneous X-rays.

Preparation of the Normal Saturated Hydrocarbons.—The hydrocarbons were prepared by reduction of the corresponding ketones by a modification of Clemmensen's process (*Ber.*, 1913, **46**, 1837).

The pure ketone (2·5—5 g.; prepared by Senderens's method) is heated under reflux on the water-bath with 50 g. of amalgamated zinc and five successive 50 c.c. portions of equal volumes of concentrated hydrochloric acid and alcohol saturated at room temperature with hydrogen chloride. For rapid reduction it is essential to have a vigorous evolution of hydrogen. When the reaction slackens, the mixture is cooled, the liquor decanted, and a further 50 c.c. of the acid mixture added to the solid. Five such treatments are usually sufficient. The total time required is about 3 hours. The hydrocarbon is purified by treatment with warm concentrated sulphuric acid and crystallised from alcohol or benzene. The yield is almost theoretical.

Discussion of the Results.—It has been pointed out in the introduction that the reflecting power for X-rays of the hydrocarbons is of the same order of magnitude as that of the fatty acids, esters, and alcohols. The conclusion was drawn that the chain in these compounds has a predominant influence on their reflecting power. The spectra obtained from the hydrocarbons are very similar to those obtained from the substances previously investigated. One set of lines belongs to a comparatively large spacing. This spacing, d_1, increases proportionally to the number of carbon atoms in the substance. Another set of lines can be related to spacings which

TABLE I

n-Hydrocarbon.	Formula.	M. p.	Main spacing. $d_1.$	Side spacings.					Ketone used.
				$d_2.$	$d_3.$	$d_4.$	$d_5.$	$d_6.$	
Heptadecane	$C_{17}H_{36}$	23°	24·3	4·25	3·93	—	2·54	2·32	Methyl n-pentadecyl.
Octadecane	$C_{18}H_{38}$	28	25·9	—	4·0	—	—	—	Ethyl n-pentadecyl.
Nonadecane	$C_{19}H_{40}$	32	26·9	4·22	3·84	—	2·52	2·25	Methyl n-heptadecyl.
Eicosane	$C_{20}H_{42}$	37	28·0	—	3·9	—	—	—	Ethyl n-heptadecyl.
Heneicosane	$C_{21}H_{44}$	41	29·4$_5$	4·17	3·77	3·01	2·50	2·25	Propyl n-heptadecyl.
Tricosane	$C_{23}H_{48}$	47	32·2	—	—	—	—	—	Di-n-undecyl.
Tetracosane	$C_{24}H_{50}$	51	33·0$_5$	4·18	3·80	3·02	2·50	2·25	Hexyl n-heptadecyl.
Heptacosane	$C_{27}H_{56}$	59·5	37·1	4·17	3·77	3·01	2·51	2·25	Di-n-tridecyl.
Hentriacontane	$C_{31}H_{64}$	69	43·0	4·14	3·74	2·99	2·49	2·21	Di-n-pentadecyl.
Pentatriacontane	$C_{35}H_{72}$	74	47·7	—	—	—	—	—	Di-n-heptadecyl.
			$d'_1.$				Side spacings.		
Octadecane, second form		—	23·9	4·58	3·80	3·66	2·61	—	2·05
Eicosane ,, ,,		—	26·2	4·63	3·82	3·61	2·59	2·12	2·03

The spacings are given in Ångström units.   1 Å.U. = 10^{-8} cm.   The measurements are only approximate

The side spacings of tricosane and pentatriacontane have not been measured.

The side spacings of the first form of octadecane and eicosane were not well defined.

are almost independent of the number, N, of carbon atoms.   These independent or side spacings have been investigated separately by a transmission method.   The two strongest lines in the side spacing group show a slight shift away from the central line on the photograph as the number of carbon atoms increases.   The side spacings d_2 and d_3 show, therefore, a slight decrease with increasing number of carbon atoms.   This means that the transverse dimensions of the

FIG. 1.

Number of carbon atoms.
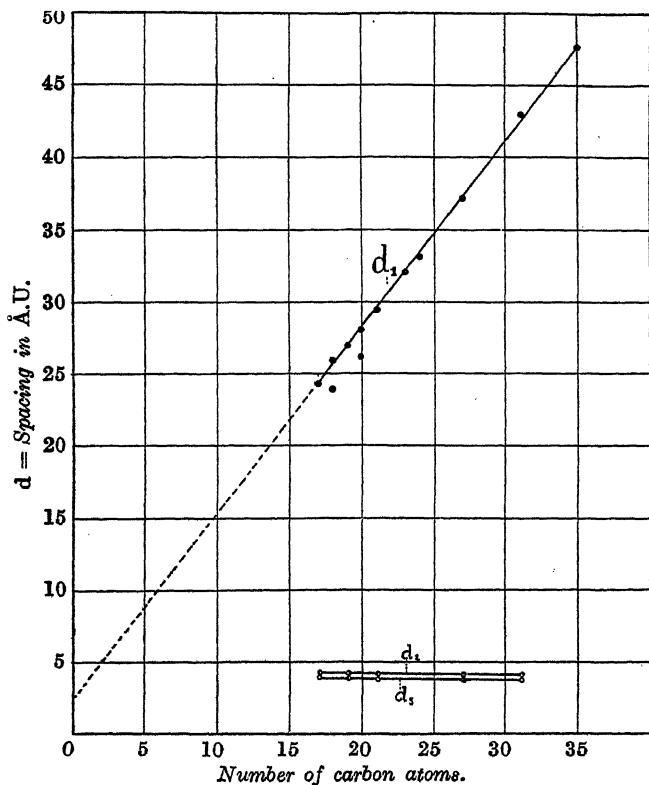
unit cell are also to a small extent a function of N.*   The numerical data are given in Table I.   A large number of lines were found which belong to the side spacing group; only the five strongest, d_2, d_3, d_4, d_5, and d_6, are given in the table.   Fig. 1 shows the linear increase of d_1 with the number of carbon atoms.

The long spacings have been measured for ten different hydrocarbons, the number of carbon atoms ranging from 17 to 35.   The

* Three of the fainter lines in the side spacing group (d_4; d_5; d_6) show only a very small variation.

increase of d_1 per carbon atom was constant within the limits of experimental error. This has been observed for all the substances investigated so far. The numerical value of this increase is, in the case of hydrocarbons, very nearly 1·3 Å.U. per carbon atom, which is larger than any corresponding value for other substances and is considerably larger than one would have expected from the theory advanced by Müller and Shearer (*loc. cit.*, p. 3158).

The picture of these long chains as given in the previous paper has therefore to be modified. The experimental data available so far are insufficient for a complete discussion of the structure of any of these long-chain compounds, but the latest measurements seem to indicate that an additional variable has to be introduced to explain their behaviour. One can obviously give up the parallelism between the long axis of the chain and d_1. Another possibility consists in the introduction of several values for the diameter of the carbon atom. These points will be discussed later in a separate paper.

A further experimental result will now be described. It was observed that the spacings of the C_{18} and C_{20} hydrocarbons did not agree with the constant increase of length per carbon atom. This happened when the substances were kept at room temperature. When, however, the temperature was changed by a certain amount, another set of lines appeared on the plates. This other set of lines belonged to a long spacing which differed from the first by something like 6—7%. The existence of these two sets of lines indicates that these substances have more than one crystalline form. Each of these modifications is stable if kept within a certain temperature range. It was further noticed that one of these two long spacings agreed with the normal increase. One experiment carried out on octadecane consisted in melting the substance and giving a short exposure immediately afterwards. The photograph, which was obtained while the substance was cooling down, showed two sets of long spacings, the longer and normal being relatively strong and the other one rather weak. After the substance had cooled down to room temperature, another photograph was taken. The longer spacing had now completely disappeared. In the next experiment (with eicosane), the temperature was controlled by means of a small heater mounted on the spectrometer table. The eicosane was melted and allowed to solidify. When it assumed the transparent solid state, an X-ray photograph was taken. As the temperature fell a sudden change occurred, the solid becoming white and opaque.*

* Garner and Randall (J., 1924, **125**, 369), who have studied the phenomena which occur during the solidification of several members of the fatty acid series, conclude that an internal rearrangement takes place after the substance has gone through the transparent stage.

Eicosane, $C_{20}H_{42}.$

centre

1st   2nd   3rd   4th   side spacings

1st   2nd   3rd   4th order

$d'_1 = 26 \cdot 2$ Å.U. $d_1 = 28 \cdot 1$ Å.U.
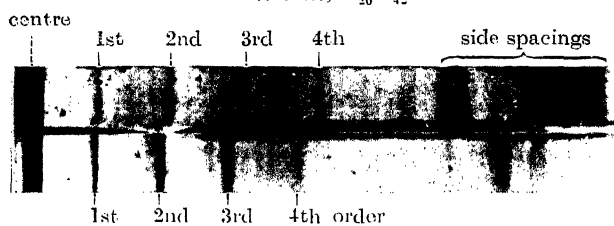
A second photograph was then taken. The results agreed with expectation. The transparent and the opaque form differed in their crystalline structure. Both the long and the side spacings were different for the two modifications. The numerical values for the two sets of long spacings were : Octadecane, $d'_1 = 23 \cdot 9$ Å.U.; $d_1 = 25 \cdot 9$ Å.U. : eicosane, $d'_1 = 26 \cdot 2$ Å.U.; $d_1 = 28 \cdot 0$ Å.U. d_1 refers to the transparent modification, d'_1 to the opaque one. Plate I shows an enlargement of the spectrograms obtained from the two modifications of eicosane. The behaviour of octadecane and eicosane is not unique. All observations on the solidification process seem to indicate that such behaviour is a general property of this type of chemical compound.

In the paper on fatty acids it was mentioned that the first, third, fifth . . . order of the long spacing give very much higher intensities of reflection than the second, fourth, sixth . . . order. The hydrocarbons behave differently. There is no alternation between the odd and the even orders. The intensity of the lines decreases gradually as the order gets higher. Dr. Shearer has shown by calculation that these facts are closely connected with the linking of the molecules in the unit cell.

Summary.

Certain normal hydrocarbons have been investigated by means of X-rays. Two typical sets of spacings are common to all the substances, one relatively large spacing, which increases linearly with the number of carbon atoms in the substance, and another set, which is very nearly independent of this number. The two strongest lines in the side spacing group coincide very closely with corresponding lines given by fatty acids, esters, and alcohols.

The increase per carbon atom of the long spacing is too large to be accounted for by the longest of the tetrahedral chains.

Two crystalline modifications have been detected for octadecane and eicosane.

LXXXIX.—*The Rotatory Dispersive Power of Organic Compounds. Part XV. Borneol, Camphor, and Camphorquinone. The Origin of Complex and Anomalous Rotatory Dispersion.*

By Thomas Martin Lowry and John Outram Cutter.

1. *Introductory.*

The three preceding papers of this series have dealt with " *simple rotatory dispersion,*" *i.e.*, with rotations which can be expressed by one term of Drude's equation, up to the limit of accuracy of the observations, and over a range of wave-lengths extending to the point at which the medium ceases to be completely transparent. Four earlier papers were devoted to the " *anomalous rotatory dispersion* " of methyl and ethyl tartrate; but the data for these esters can be expressed with similar accuracy by the same general equation when two terms of opposite sign are used instead of one. These observations had two important features in common, namely, (i) that in neither group of compounds could a band of selective absorption be detected by the methods at present available, which show only a general absorption spreading in from the inaccessible ultra-violet region; (ii) that the asymmetric system was always very simple, *e.g.*, one asymmetric carbon atom in octyl alcohol, two of identical type in the tartaric esters, and none at all in Pope's acid. The present and following papers describe an attack on more complicated systems, since the substances used (i) contain 2, 3, or 4 dissimilar asymmetric carbon atoms and (ii) exhibit a selective as well as a general absorption of light.

The investigation of these more difficult cases was undertaken without any preconceived ideas as to the complex character of the dispersion which they exhibit, or the possible relation of the rotatory dispersion to the absorption of the compounds, which was only taken up after the whole of the rotations had been measured and expressed by means of equations. These equations are, therefore, purely experimental in character, and were not biassed by theoretical considerations of any kind, except as a result of a well-founded conviction in the validity of Drude's equation in its most general form. The work was indeed begun with a mistaken expectation (based on a rough graphical analysis of a few earlier data) that the rotatory dispersion of camphor would prove to be *simple*, but might be rendered complex by the development of a new asymmetric carbon atom in the stereoisomeric

α- and α'-derivatives. The new experiments soon proved, however, the futility of this expectation, and revealed the fact that we had plunged much more deeply than we desired into the problem of complex rotatory dispersion; it is, indeed, only since the development by Lowry and Walker of the theory of "induced asymmetry" in unsaturated compounds that we have been able to form a clear picture of what was happening, or to give a plausible explanation of these very puzzling phenomena. Since these three papers will be followed by others dealing with the rotatory dispersion of unsaturated compounds, in which the same principles will be applied, it will be convenient to explain in advance the views which we hold in reference to the origin of complex and anomalous dispersion in compounds of this type.

2. *A General Theory of the Origin of Anomalous Rotatory Dispersion.*

It has recently been stated (Astbury, *Chem. and Ind.*, 1924, **43**, 332) that "no sound general theory of anomalous rotatory dispersion exists." This statement we regard as incorrect, as it has been known since 1836 that *anomalous rotatory dispersion in transparent media is produced by the superposition of two normal rotations of opposite sign and unequal dispersion.* R. W. Wood has indeed directed attention to the fact that "spurious" anomalies may occur in the region between two absorption bands, and has even suggested that the anomalous rotatory dispersion of tartaric acid may be a case of this kind, depending on the combined influence of an ultra-violet and an infra-red absorption; but this view receives no support from measurements of the rotatory dispersion of this series of compounds, since these can be expressed completely as the sum of two simple partial rotations *of which the characteristic frequencies are both in the ultra-violet region.* This type of anomaly has, in fact, never been observed in any optically-active compound. Although, therefore, we may admit the theoretical possibility of a "spurious" anomalous rotatory dispersion, even in transparent media, the explanation given by Biot in 1836 still covers the whole of the experimental data.* The only point

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* The anomaly discovered by Cotton in 1895 (*Compt. rend.*, 1895, **120**, 989, 1044; *Ann. Chim. Phys.*, 1896, [vii], **8**, 347) in the optical rotations *when passing through an absorption band* is so familiar in other optical properties and appears to be so inevitable, that, as R. W. Wood says, "there is nothing anomalous about it." It is therefore only because anomalous rotatory dispersion is observed *in transparent media,* and *at wave-lengths differing widely from those of selective absorption,* that a special explanation is called for, and this is provided by the fact that optical rotations are of two signs, whereas refractions are all of similar sign.

of controversy is therefore the origin of the two opposite partial rotations in any particular case, and not the general theory that anomalies are produced by their superposition.

It is, however, necessary to emphasise the fact that *no theoretical significance whatever can be attached to the distinction between normal and anomalous rotatory dispersion*, when both are of a type which can be represented by a Drude equation containing two terms of opposite sign,* since a minute change in the rotation-constants of the equation, *e.g.*, as a result of an unimportant change of temperature or of concentration, may suffice to alter the type of dispersion from normal to anomalous,† or *vice versa*.   It is therefore of primary importance to determine (i) whether the dispersion can be expressed by one term of Drude's equation, or requires two or more terms of this equation to represent it, *i.e.*, whether the dispersion is simple or complex, and (ii) in the case of a two-term equation, whether the partial rotations are *of similar sign* or *of opposite signs*, since these are much more fundamental facts than a mere reversal of sign in the algebraic sum of two opposite partial rotations, which is all that is implied in the change from normal to anomalous dispersion.   Moreover, even on the experimental side, the classification of dispersions as "normal" and "anomalous" is no easier than the classification as "simple" and "complex," ‡ which has been put forward to supplement and not to replace the older system.

3. *Methods of Superposing Opposite Partial Rotations.*

As long ago as 1914, in discussing the origin of the anomalous rotatory dispersion of ethyl tartrate, it was suggested by one of us (*Trans. Faraday Soc.*, **10**, 100), in complete agreement with the views of Tschugaev, that anomalies such as these could be produced by superposing the opposite rotations of (i) *two molecules*, (ii) *two radicals* in one molecule, or (iii) *two electrons*, *e.g.*, in one molecule or in one crystal.   It is now possible to divide these three classes further into six principal types as follows :

(a) *Optical superposition of two separate media*, as observed by

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* See footnote, p. 608.

† This distinction hinges on the question whether the dispersion curve just crosses or just fails to cross the axis of zero rotation.

‡ Thus $[a] = 18 \cdot 0/(\lambda^2 - 0 \cdot 03) - 19 \cdot 0/(\lambda^2 - 0 \cdot 06)$ would give a *normal* dispersion, whilst $[a] = 19 \cdot 0/(\lambda^2 - 0 \cdot 03) - 18 \cdot 0/(\lambda^2 - 0 \cdot 06)$ would give an *anomalous* dispersion.   Since the anomalies would all be in the infra-red, it would be just as difficult to distinguish experimentally between the normal and the anomalous dispersion as it is to distinguish between a simple and a complex dispersion when the latter is produced by two partial rotations of the same sign and with dispersion constants of similar magnitude.

Biot in 1836 (*Compt. rend.*, 2, 543), on balancing a column of lævo-rotatory turpentine against a column of dextrorotatory oil of lemon.

(b) *Mixing of two fluid media*, as realised by Biot (*loc. cit.*) on mixing oil of turpentine and oil of lemon in a single tube; by von Wyss (*Wied. Ann. Phys. Chem.*, 1888, [ii], 33, 567) by mixing turpentine and camphor in the same solution; and by Tschugaev (*Z. physikal. Chem.*, 1911, 76, 469) by mixing lævorotatory menthone with dextrorotatory *iso*menthone. In all these cases, the two oppositely-active molecules were stable in the solution, and not interconvertible under the conditions then prevailing.

(c) *Formation of two molecular types from one optically-active compound*, as suggested by Arndtsen in 1858 (*Ann. Chim. Phys.*, 54, 421). One of these types will usually be the same as in the solid crystalline phase (L. Longchambon, *Thesis*, Paris, 1923; *Compt. rend.*, 1924, 178, 951; Lowry and Austin, *Nature*, 1924, 114, 430), but the other may be produced either (i) *by association with the solvent*, including the formation of *molecular compounds*, of *hydrated* or *solvated ions*, and of products of *reversible hydrolysis* or *esterification*; (ii) *by polymerisation, dissociation*, or *isomeric change of the solute*. In the absence of a solvent, however, only cases of group (ii) are possible.

(d) *Presence of oppositely-active radicals in one molecule*, as in the *l*-menthyl *d*-camphorsulphonate of Tschugaev (*Trans. Faraday Soc.*, 1910, 10, 73). It is open to discussion whether the formation of salts from oppositely-active acids and bases should come under this heading, or whether the active ions should be treated as independent molecules, and their solutions regarded as mixtures of type (b) above.

(e) *Induced asymmetry in unsaturated molecules.* It has recently been suggested (Lowry and Walker, *Nature*, 1924, 113, 565) that an unsaturated group in an asymmetric molecule, *e.g.*, the $>C{=}O$ group in camphor, may acquire an induced asymmetry and thus itself become optically active. This hypothesis has the effect of transferring a large number of cases of anomalous dispersion from Drude's class (f) below to a variant of Tschugaev's class (d) above, since the two opposite partial rotations, instead of being attributed merely to the existence of two natural frequencies in a single molecule, are assigned to different radicals or groups of electrons in the molecule. These cases then differ from Tschugaev's type (d) only in that the presence of a low-frequency term in the dispersion equation is ascribed to the *induced* asymmetry of an unsaturated group (in a molecule already containing a centre of fixed asymmetry) instead of a second centre of *fixed* asymmetry in the molecule.

(f) *Existence of two natural frequencies* (i) *in a single crystal,*
(ii) *in a single molecule.* (i) *Crystals with two natural frequencies.*
Drude regarded anomalous rotatory dispersion as due to the super-
position of the partial rotations of two electrons moving in an
asymmetric field, with unequal periods of vibration, and in spirals
of opposite sign. No case of anomalous rotatory dispersion has
yet been recorded in a transparent crystalline medium; but since
the two ultra-violet terms in the dispersion-equation of quartz
are of opposite sign, it is merely an accident that the relative
magnitude of the two partial rotations is such as not to give rise
to anomalous dispersion; * all the common anomalies would indeed
appear immediately if the high-frequency term were multiplied
by 4. In the case of quartz, Drude's opposite types of asym-
metrically-moving electrons must obviously exist *in a single crystal
lattice* and *in a single type of molecule,* so that none of the first
three methods (a), (b), and (c) of explaining its " quasi-anomalous "
dispersion can be applied. Since, however, we may hope ultimately
to be able to assign the two ultra-violet terms to two different
asymmetric complexes in the crystal-lattice (*e.g.,* one depending
mainly on a dissymmetric arrangement of the silicon atoms and
of the electrons associated with them, and the other on a dis-
symmetry of the oxygen groups in the crystal aggregate), we can
scarcely expect to maintain class (f) (i) as a totally distinct type of
anomalous dispersion. The complex dispersion of quartz appears
indeed to differ from type (d) only in that the asymmetric radicals
of Tschugaev's molecules are stable and survive dissolution, whilst
those of quartz are only found in the polymerised aggregates of
the crystal, and disappear when these aggregates are broken up.

(ii) *Molecules with two natural frequencies.* It was obviously
possible, on Drude's theory, for two dissimilar types of asym-
metrically-moving electrons to appear in the same molecule as
well as in the same crystal, giving rise to two absorption bands

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* Such cases would be described accurately as " potentially anomalous."
Hunter, however, applies this term to the " normal " portions of a totally
anomalous curve, *i.e.,* to that half of the curve, lying on one side of the
maximum, in which a increases as λ diminishes, so that $da/d\lambda$ is negative.
It should be noticed that this definition is unsatisfactory, in that it includes
a section of the curve, between the maximum and the point of inflexion, in
which $da/d\lambda$ decreases in magnitude instead of increasing as λ diminishes,
so that its anomalous character is obvious rather than merely potential.
In order to avoid ambiguity, it is suggested that the term *quasi-anomalous*
should be applied to cases such as quartz, in which a *complex dispersion
is produced by partial rotations of opposite sign,* but of such a character that
a, $da/d\lambda$, and $d^2a/d\lambda^2$ are of the same sign throughout the region of trans-
parency lying on the " long wave-length " side of the nearest absorption
band.

and to two partial rotations of corresponding frequencies. In the case of organic compounds, however, there are good experimental reasons for ascribing each absorption band to some particular radical in the molecule. The corresponding partial rotations may therefore also be ascribed to these radicals, a view that has already been urged under (e) in the case of unsaturated radicals. In all such cases, the dispersion would then again be of the same general type as (d) or Tschugaev's class. A possible exception, in which the transfer to class (d) could not be effected, would arise if it could be proved that a single asymmetric centre possessed two natural frequencies and gave rise to two bands; but the real existence of such a case, and the consequent necessity of recognising a separate class (f) (ii), is at present a matter of pure speculation. The idea that these two frequencies could give partial rotations of opposite sign, and so produce a totally anomalous dispersion, is even less plausible, and therefore need not be considered at present.

Since any of these six methods of superposing opposite partial rotations may give rise to a complex or an anomalous dispersion, there is no justification for singling out any one of them as a unique cause of anomalous rotatory dispersion. Thus the recent work of Longchambon provides further confirmation of the view that the anomalous dispersion of tartaric acid and its esters should be assigned to class (c). On the other hand, the quasi-anomalous dispersion of borneol, with three fixed centres of asymmetry, is assigned to class (d); and that of camphor to class (e), although some further complexity may be introduced by the formation of unstable " molecular compounds " of camphor with the solvent. Again, the complex dispersion, which so often appears on passing from an optically-active alcohol to its esters, may be due to the development of a partial rotation of opposite sign in the carbonyl radical of the unsymmetrical molecule, just as in the case of camphor. Finally, the complex dispersion of quartz must be assigned provisionally to class (f) (i), until it is possible to distinguish the asymmetric centres which give rise to the various partial rotations.

4. *Discussion of Experimental Results.*

(a) *Scope of the Measurements.*—The present paper includes measurements of the rotatory dispersion of camphor in benzene, *cyclo*hexane, and acetone, and of borneol and camphorquinone in benzene. The camphor was sublimed, and crystallised from *cyclo*hexane, without change of rotatory power; the borneol was crystallised three times from benzene, and the camphorquinone to constant melting point at 198°.

The solvents were selected mainly with a view to adequate

purification, e.g., in the case of benzene and cyclohexane, by freezing until the melting points were constant at 5·54° and 6·28° and the boiling points were 80·2° and 80·9° (corr.); in the case of acetone, by forming a compound with sodium iodide (J., 1913, **103**, 1255). Benzene was used most frequently, since it is easily dried, and gives solutions of a high degree of concentration; it was only at a later stage, when it was desired to compare the rotatory dispersion with the selective absorption of the solute, that this choice was found to be disadvantageous. It is, however, remarkable that *a solution of camphor in benzene is less opaque to ultra-violet rays than a solution in* cyclohexane (compare Gifford and Lowry, *Proc. Roy. Soc.*, 1923, **104**, 434), which transmits very little ultra-violet light. This greater transparency, which made it necessary to replace the glass prisms of the spectrograph by quartz, in order to reach the working limit of transmission of the solution in benzene, is perhaps due to a mutual saturation of the " residual affinities " of the camphor and benzene.

The results recorded vary considerably in value, according to the concentration of the solution, the number and range of wavelengths used, and the labour incurred in repeating the readings in order to diminish the errors of observation. Thus, Table I, for a concentrated solution in benzene, which includes 41 wave-lengths from 6708 to 3599 Å.U., may be regarded as a " standard " series, in which every effort was made to secure the highest degree of accuracy that can be reached with our present equipment and method, since the visual observations are based on two series of readings with solutions prepared independently by weight, and four such solutions were used for the photographic readings. On the other hand, Table V, for camphorquinone in benzene, includes only 9 wave-lengths in the red to green portion of the spectrum, which is all that can be used for visual readings of a strong solution. The other tables are intermediate in value between these two extremes.

(b) *Form of the Curves.*—All the equations were in the first instance empirical, the only object being to find an algebraical expression which would fit the experimental data. Any theoretical deductions are therefore an after-thought. It is, however, noteworthy that the " simple " equation for camphorquinone has a dispersion-constant, $\lambda^2 = 0·2235$, $\lambda = 4730$ Å.U., which corresponds closely with the maximum of selective absorption, although this wave-length is 30 to 80 Å.U. longer than that of the uncorrected position of the " head of the absorption-band." This equation appears, therefore, to have a real theoretical significance, although the simplicity of the observed rotatory dispersion may

perhaps be due to the cancelling out of two high-frequency partial rotations (compare J., 1924, **125**, 2520). In the same way, the two-term equation, which expresses in so satisfactory a manner the rotatory power of camphor in benzene, appears to have a real physical meaning, since the low-frequency term has a dispersion-constant, $\lambda^2 = 0.08720$, $\lambda = 2950$ Å.U., which again corresponds with a wave-length about 70 Å.U. greater than that of the observed " head " (at 2880 Å.U.) of the absorption band of a thin film of camphor in benzene (J., 1924, **125**, 1923). In view, however, of the difficulty of analysing the high-frequency component of a dispersion which is already dominated by a partial rotation of low-frequency, we prefer to leave open the question whether this component is really simple, *e.g.*, whether the characteristic frequencies of the two fixed centres of asymmetry, to which this term must be attributed, are identical or merely similar in magnitude.

The remaining equations contain only three constants, since one of the dispersion-constants has been omitted in precisely the same way as in Drude's equation for quartz.* Equations such as these can have no precise theoretical significance, since it has already been established that the two dispersion constants of a four-constant equation can often be varied appreciably without producing any important alteration in the form of the curve,† provided that they are altered simultaneously, *e.g.*, in such a way that their *sum* is kept constant ‡ (Lowry and Dickson, J., 1915, **107**, 1186). It must therefore be assumed that *the low-frequency dispersion-constant of a two-term equation is vitiated whenever the high-frequency dispersion-constant is neglected.* This possibility

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* It is noteworthy that a three-constant equation often gives results which cannot be improved by using a fourth constant. This would be expected in all cases in which the high-frequency term is small in magnitude; but in other cases it may be suspected that a term of the type k/λ^2 indicates the presence of two partial rotations of opposite sign, exactly as in the case of a pseudo-simple dispersion which nearly obeys Biot's law (J., 1924, **125**, 2519).

† The absolute values of these constants are therefore obviously much less exact than the values given for the purpose of calculation.

‡ The two-term equation can be rewritten thus :

$$[a] = \frac{k_1}{\lambda^2 - \lambda_1{}^2} + \frac{k_2}{\lambda^2 - \lambda_2{}^2} = \frac{\lambda^2(k_1 + k_2) - (k_2\lambda_1{}^2 + k_1\lambda_2{}^2)}{\lambda^4 - \lambda^2(\lambda_1{}^2 + \lambda_2{}^2) + \lambda_1{}^2\lambda_2{}^2}.$$

Since we are considering the region in which λ^2 is greater than $\lambda_1{}^2$ or $\lambda_2{}^2$, the terms in the numerator and denominator are arranged in order of decreasing magnitude. As a first approximation, the rotation will be altered least if we keep $(k_1 + k_2)$ constant in the numerator and $(\lambda_1{}^2 + \lambda_2{}^2)$ constant in the denominator. This relation is valid whether k_1 and k_2 are of the same sign or of opposite signs.

<div align="center">

TABLE I.

Rotations of d-*Camphor in Benzene* (*conc. solution*).

33·827 Gms. of camphor in 100 gms. of solution.
Density 0·90793.   Length of tube 6 dcm.

$[\alpha] = 0.5427\ a.\quad [M] = 1.5213\ [\alpha].$

$$[\alpha] = \frac{29.384}{\lambda^2 - 0.08720} - \frac{20.138}{\lambda^2 - 0.05428}$$

</div>

(a) *Visual Readings.*

Wave-length.	Specific rotations.			Wave-length.	Specific rotations.		
	Obs.	Cal.	Diff.		Obs.	Cal.	Diff.
Li 6707·8	29·78°	30·12°	—0·34°	Fe 4595	108·5°	108·8°	—0·3°
Cd 6438·5	33·85	33·88	—0·03	4500	119·4	119·0	+0·4
Zn 6362·3	35·10	35·09	+0·01	4408	130·2	130·6	—0·4
Na 5893·0	44·01	44·27	—0·26	4332	141·1	141·3	—0·2
Hg 5790·7	46·75	46·80	—0·05	4266	152·0	152·3	—0·3
Cu 5782·2	46·85	47·02	—0·17	4208	162·8	163·1	—0·3
Hg 5769·6	47·29	47·34	—0·05	4157	173·6	173·4	+0·2
Cu 5700·2	48·95	49·22	—0·27	4104	184·5	185·3	—0·8
Hg 5460·7	56·72	56·72	±	4055	195·4	197·6	—2·2
Cu 5218·2	66·45	66·41	+0·04	4022	206·2	206·8	—0·6
Cu 5153·3	69·52	69·47	+0·05	3986	217·1	217·5	—0·4
Cu 5105·5	71·95	71·85	+0·10	3953	227·9	228·0	—0·1
Cu 5085·8	73·01	72·88	+0·13	3919	238·8	239·9	—1·1
Zn 4810·5	90·21	90·11	+0·10	3892	249·6	250·0	—0·4
Cd 4799·9	92·23	90·90	+1·33	3864	260·5	261·4	—0·9
Zn 4722·2	97·37	97·07	+0·30	3838	271·3	272·4	—1·1
				3815	282·2	283·0	—0·8
(b) *Photographic Readings.*				3793	293·0	293·8	—0·8
Fe 5233	65·1	65·7	—0·6	3754	314·7	314·6	+0·1
5042	76·0	75·3	+0·7	3640	390·7	391·6	—0·9
4860	87·0	86·8	+0·2	3599	428·7	426·7	+2·0
4707	97·7	98·3	—0·6				

appears to have been overlooked by Pickard and Hunter (J., 1923, **123**, 434) when they attempted to correlate the absorption band of nonyl nitrite with the low-frequency dispersion-constant of a two-term equation *containing only three constants.* Since, however, they also made no correction for the displacement of the head of the absorption-band relative to the real maximum of selective absorption, no important discrepancy was observed, as the two errors are in the same direction. The view set out above receives strong confirmation from the fact that, although the maximum of absorption occurs at exactly the same wave-length in solutions of camphor in benzene and in *cyclo*hexane (J., 1924, **125**, 1923), the low-frequency dispersion-constant in the *three*-constant equation for the solution in *cyclo*hexane, $\lambda^2 = 0.09114$, $\lambda = 3020$ Å.U., corresponds to a wave-length which is greater by 70 Å.U. than in the case of a *four*-constant equation for the solution in benzene.

(c) *Optical Activity of the Ketonic Group.*—When the experiments now described were begun, we accepted the current view that

TABLE II.

Rotations of d-*Camphor in Acetone at* 20°.

29·8090 Gms. of camphor in 100 gms. of solution.
Density 0·8405. Length of tube 6 dcm.

$$[a] = 0.6652\ a.\quad [M] = 1.5213\,[a].$$
$$[a] = \frac{18.022}{\lambda^2 - 0.09363} \quad 7.1324$$

(a) *Visual Readings.*

Wave-length.	Specific rotations.			Wave-length.	Specific rotations.		
	Obs.	Cal.	Diff.		Obs.	Cal.	Diff.
Li 6707·8	34·78°	34·72°	+0·06°				
Cd 6438·5	38·98	37·62	+1·36	(b) *Photographic Readings.*			
Zn 6362·3	40·32	40·30	+0·02	Fe 4982	86·5°	87·9°	−1·4°
Na 5893·0	50·51	50·52	−0·01	4761	99·8	101·1	−1·3
Hg 5780·1	53·69	53·60	+0·09	4495	133·0	130·1	+2·9
Cu 5782·2	53·57	53·54	+0·03	4397	146·4	143·9	+2·5
Cu 5700·2	56·31	55·96	+0·35	4315	153·0	155·5	−2·5
Hg 5460·7	64·25	64·20	+0·05	4234	173·0	170·6	+2·4
Cu 5218·2	74·61	74·68	−0·07	4165	184·6	182·7	−1·9
Ag 5209·1	75·04	75·12	−0·08	4096	199·6	200·6	−1·0
Cu 5153·3	77·81	77·84	−0·03	4054	212·9	211·5	+1·4
Cu 5105·5	80·33	80·53	−0·20	4005	226·2	225·0	−1·2
Cd 5085·8	81·53	80·95	+0·58	3941	246·0	246·1	−0·1
Zn 4810·5	99·87	99·98	−0·11				
Cd 4799·9	100·68	100·82	−0·14				
Zn 4722·2	106·89	107·66	−0·77				

optical activity is a property of the total molecule, and that the picking out of certain atoms as " asymmetric " is merely a convenient way of recording the asymmetry of the molecule as a whole. We have abandoned this view for purely experimental reasons, although in doing so we have taken up an attitude which is more in harmony with modern physical conceptions, since these attribute optical activity to one or more groups each comprising *four pairs of coupled electrons* (Born, *Physikal. Z.*, 1915, **16**, 251; *Ann. Physik*, 1912, [iv], **55**, 177), instead of to an indefinite number of electrons oscillating in spiral paths. Our principal reason for regarding the optical effects as localised is, however, the fact that the dispersion-equations for camphor and its derivatives are haunted by a low-frequency term *the period of which is definitely characteristic of the ketonic group.* We therefore assign this partial rotation to the ketonic group, which is proved to be asymmetric by the unequal yields of the two stereoisomeric products which are obtained when the double bond is converted into two single bonds. This absence of symmetry in a double bond has already been proved in the camphor series by the unsymmetrical reduction of camphor to borneol and *iso*borneol (Montgolfier, *Ann. Chim. Phys.*, 1878, **188**, 5), and of its oxime to bornylamine and neobornylamine (Forster, J., 1898, **73**, 386), and (less directly) by its

TABLE III (a).	TABLE III (b).

Rotations of d-*Camphor* in cyclo*Hexane* at 20°. | Rotations of Borneol in Benzene at 20°.

23·1820 Gms. of camphor in 100 gms. of solution. Density 0·81525. Length of tube 6 dcm.

22·8550 Gms. of borneol in 100 gms. of solution. Density 0·89903. Length of tube 6 dcm.

$[\alpha] = 0.8820\ a.$ $[M] = 1.5213\ [\alpha].$
$$[\alpha] = \frac{20.007}{\lambda^2 - 0.09114} - \frac{9.2255}{\lambda^2}.$$

$[\alpha] = 0.8111\ a.$ $[M] = 1.5415\ [\alpha]$
$$[\alpha] = \frac{9.7866}{\lambda^2 - 0.07442} - \frac{3.2862}{\lambda^2}.$$

Specific Rotations. | Specific Rotations.

Wave-length.	Obs.	Cal.	Diff.	Obs.	Cal.	Diff.
Li 6707·8	36·74°	35·38°	+1·3$_6$°	18·78°	18·77°	+0·01°
Cd] 6438·5	39·63	39·58	+0·0$_5$	20·95	20·85	+0·10
Zn 6362·3	41·04	41·00	+0·0$_4$	21·53	21·50	+0·03
Na 5893·0	52·25	51·55	+0·7$_0$	26·28	26·48	−0·20
Hg 5780·1	54·77	54·73	+0·0$_4$	27·93	27·84	+0·09
Cu 5782·2	55·04	54·68	+0·3$_6$	27·88	28·70	−0·18
Cu 5700·2	56·53	56·53	±	29·11	28·95	+0·16
Ag 5468·6	—	—		32·62	33·74	−1·12
Hg 5460·7	65·44	65·64	−0·2$_0$	32·55	32·40	+0·15
Cu 5218·2	76·41	76·56	−0·1$_5$	37·34	37·39	−0·05
Ag 5209·1	—	—	—	37·47	37·58	−0·11
Cu 5153·3	79·38	79·97	−0·5$_9$	38·77	38·82	−0·05
Cu 5105·6	82·18	81·80	+0·3$_8$	39·90	39·94	−0·04
Cu 5085·8	83·28	83·77	−0·4$_9$	40·32	40·41	−0·09
Zn 4810·5	102·58	102·77	−0·1$_9$	48·05	48·13	−0·08
Cd 4799·0	103·57	103·64	−0·0$_7$	48·43	48·48	−0·05
Zn 4722·2	109·98	110·33	−0·3$_5$	51·28	51·13	+0·15
Hg 4358·3	153·65	153·92	−0·2$_7$	68·46	67·41	+1·05

TABLE IV.

Rotations of Camphorquinone in Benzene at 20°.

15·069 Gms. of camphorquinone in 100 gms. of solution. Density 0·90290. Length of tube 6 dcm.

$[\alpha] = 1.225\ a.$ $[M] = 1.6611\ [\alpha].$
$$[\alpha] = \cdot\ \frac{13.170}{\lambda^2 - 0.22352}$$

Specific Rotations.

Wave-length.	Obs.	Cal.	Diff.
Li 6707·8	− 58·26°	− 58·16°	−0·10°
Cd 6438·5	− 68·60	− 68·93	+0·33
Zn 6362·3	− 72·66	− 72·64	−0·02
Na 5893·0	−105·98	−106·42	+0·44
Cu 5782·2	−117·96	−118·93	
Hg 5780·1	−118·42	−119·10	
Cu 5700·2	−128·21	−127·65	
Ag 5468·6	−174·83	−174·36	−0·47⎫
Hg 5460·7	−176·40	−176·34	−0·06⎭

unsymmetrical bromination to an equilibrium mixture of α- and α'-bromocamphor in the ratio 8 : 1. Since the two links of a double bond in an asymmetric compound are clearly unequal

rom the chemical point of view, it would be absurd to pretend hat they must be equal from the physical point of view, and no .dditional justification need therefore be given for using this con- ,eption in order to explain the optical properties of camphor or)f the other unsaturated compounds now under investigation.

5. *Summary.*

(*a*) The rotatory power of a strong solution of camphor in)enzene, for 41 wave-lengths in the visible and ultra-violet regions, ,an be represented very satisfactorily by the equation

$$[\alpha] = 29 \cdot 384/(\lambda^2 - 0 \cdot 0872) - 20 \cdot 138/(\lambda^2 - 0 \cdot 05428).$$

The low-frequency term corresponds to a wave-length 70 Å.U. ;reater than the observed " head of the band " at 2880 Å.U. of ι film of camphor in benzene and is probably identical with the :eal maximum of selective absorption. The low-frequency dis-)ersion constant of a three-constant equation for a solution of ;amphor in *cyclo*hexane shows a further displacement of 70 Å.U., probably as a result of neglecting the high-frequency dispersion- ;onstant, since the maximum of absorption is not displaced by the change of solvent.

(*b*) The rotatory power of borneol in the visible spectrum can be expressed by the equation

$$[\alpha] = 9 \cdot 7866/(\lambda^2 - 0 \cdot 07442) - 3 \cdot 286/\lambda^2.$$

(*c*) The rotatory power of camphorquinone, over the narrow range of transparency in the visible spectrum, can be expressed by the equation

$$[\alpha] = - 13 \cdot 170/(\lambda^2 - 0 \cdot 022352),$$

where the dispersion-constant again corresponds with a wave- length, slightly larger (30 to 80 Å.U.) than the observed " head of the band," which is probably identical with the real maximum of selective absorption.

(*d*) The origin of anomalous rotatory dispersion is discussed, and the term " quasi-anomalous " is defined.

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XC.—*The Chemistry of the Three-carbon System. Part III. The αβ–βγ Change in Unsaturated Acids.*

By GEORGE ARMAND ROBERT KON and REGINALD PATRICK LINSTEAD.

IN the first two papers of this series (J., 1923, **123**, 1361, 2440) it was pointed out that tautomerism, as defined there, occurs in compounds containing a three-carbon system whenever one terminal carbon atom of this system carries a suitable electronegative " activating " group and the two remaining carbon atoms form part of an alicyclic ring or a *gem*-grouping.

$$\begin{matrix} -CH_2 \\ -CH_2 \end{matrix}\!\!> C\!:\!CHX \qquad\qquad \begin{matrix} -CH_2 \\ -CH \end{matrix}\!\!> C\!\cdot\!CH_2X$$

αβ-form.   βγ-form.
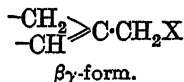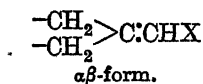
The cause underlying this phenomenon was thought to be the competition between two opposed factors—the effect of the ring stabilising the βγ-form, and the tendency to produce a conjugated system favouring the αβ-form.

In considering tautomeric systems of this kind—and this applies equally well to keto-enol tautomerism—it is necessary clearly to differentiate between two fundamental properties which characterise them, *viz.*, the degree of mobility of the system and the actual point of equilibrium attained under a given set of conditions. Thus, a system may possess a high degree of mobility and the substance will then occur in one form only, doubtless consisting of an equilibrium mixture containing a large proportion of one individual but reacting in the αβ- or the βγ-form according to circumstances; or both forms may be isolated and be converted one into the other by more or less drastic treatment. *cyclo*Hexenylacetone and ethyl α-cyano*cyclo*hexylideneacetate are good examples of the mobile type (see Part I, *loc. cit.*), whilst the unsaturated acids studied by Fittig supply a classical example of a system which is only mobile in the presence of a powerful reagent; the isomeric αβ- and βγ-acids are otherwise quite distinct and readily separated.

The point of equilibrium, on the other hand, depends only on the relative stability of the two forms and is independent of the rate of conversion. Thus, whilst both the mobile substances mentioned above are only obtainable in one form,* the former has normally the βγ-, the latter the αβ-structure. Again, in Fittig's acids, which are static under ordinary conditions, the equilibrium in the presence of reagents is strongly on the side of the αβ-form,

* It is proposed in the near future to study the possibility of obtaining the two forms of substances of this type.

and this property is so general in the unsaturated acids that it has come to be known as Fittig's rule. The object of the present communication is to examine the point of equilibrium in certain unsaturated acids possessing but a small degree of mobility and therefore particularly suited to our purpose, and to arrive, if possible, at a more trustworthy generalisation.

Up to the present, the principal exception to Fittig's rule was *cyclo*hexylideneacetic acid, which passes completely and irreversibly into its βγ-isomeride on treatment with concentrated alkali (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1081). An explanation of this change has already been suggested, based on the tendency of the double bond to migrate into the ring (Birch, Kon, and Norris, Part I of this series, *loc. cit.*). Some of the cases described by Blaise and Luttringer (*Compt. rend.*, 1905, **140**, 148) might be included under this category, but their acids underwent the αβ–βγ change under the influence of sulphuric acid, which further transformed the products into lactones and thus removed them from the sphere of the reaction. The same may be said of the acids studied by Fichter, Kiefer, and Bernoulli (*Ber.*, 1909, **42**, 4710), in addition to which it is very doubtful whether the latter authors were dealing with pure materials in all cases (see p. 618).

Some further cases of the αβ–βγ change have now been studied and we have found that several acids of the general formula (I) will pass into their βγ-isomerides (II) on treatment with alkali; the scheme also applies when the *gem*-dialkyl grouping is replaced

$$\text{(I.)} \quad \underset{\text{R·CH}_2}{\overset{\text{R·CH}_2}{>}}\text{C:CH·CO}_2\text{H} \qquad \underset{\text{R·CH}}{\overset{\text{R·CH}_2}{>}}\text{C·CH}_2\text{·CO}_2\text{H} \quad \text{(II.)}$$

by a *cyclo*hexane or *cyclo*pentane ring. Thus *cyclo*pentylideneacetic acid (III), like its *cyclo*hexane analogue, is very rapidly and completely converted into its isomeride (IV), not only by alkalis,

$$\text{(III.)} \quad \underset{\text{CH}_2\text{·CH}_2}{\overset{\text{CH}_2\text{·CH}_2}{>}}\text{C:CH·CO}_2\text{H} \qquad \underset{\text{CH}_2\text{--CH}}{\overset{\text{CH}_2\text{·CH}_2}{>}}\text{C·CH}_2\text{·CO}_2\text{H} \quad \text{(IV.)}$$

but also by mineral acids; it is, in fact, a matter of some difficulty to prepare the pure αβ-acid. However, the chief interest of the present investigation centres on ββ-diethylacrylic acid (V) and its isomeride (VI), because these acids have already been studied by Fichter, Kiefer, and Bernoulli (*loc. cit.*).

$$\underset{\text{Et}}{\overset{\text{Et}}{>}}\text{C:CH·CO}_2\text{H} \qquad \underset{\text{CHMe}}{\overset{\text{Et}}{>}}\text{C·CH}_2\text{·CO}_2\text{H} \qquad \underset{\text{CHMe--O}}{\overset{\text{CEt·CH}_2\text{·CO}}{|}}$$

$$\text{(V.)} \qquad\qquad\qquad \text{(VI.)} \qquad\qquad\qquad \text{(VII.)}$$
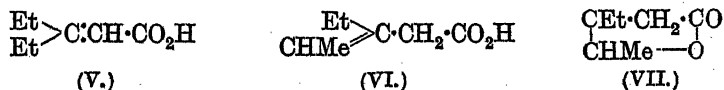
These authors describe an acid (b. p. 217—218°; *p*-toluidide, m. p. 95°) to which, from its method of formation, they assigned

the αβ-formula (V). They observed that this acid passed on treatment with sulphuric acid (with or without previous equilibration with alkali) into β-ethylvalerolactone (VII). From this and from a similar observation on the methylethyl acid, they concluded that ββ-dialkylacrylic acids pass into lactones on treatment with sulphuric acid (Fittig's method of separating αβ- from βγ-acids), probably with the intermediate formation of a βγ-acid such as (VI).

The preparation of Fichter's acid by the elimination of water from ethyl β-hydroxy-ββ-diethylpropionate, followed by hydrolysis, was carefully repeated, and an acid giving a p-toluidide, m. p. 94°, was readily obtained and further characterised by the preparation of its *amide*, m. p. 113—114°. Its physical and chemical properties, however, did not agree with the constitution assigned to it; on oxidation of its ester with ozone and decomposition of the ozonide with water, acetaldehyde and not diethyl ketone was obtained, showing conclusively that the acid had the βγ-formula (VI). In accordance with this, both the acid and its ester showed a normal molecular refraction.

It appeared certain that Fichter and his collaborators were dealing with the βγ-acid throughout and efforts were made to prepare its isomeride. This was achieved by treating β-hydroxy-ββ-diethylpropionic acid, $Et_2C(OH)\cdot CH_2\cdot CO_2H$, with acetic anhydride, when an unsaturated acid was formed in rather poor yield (mainly owing to the formation of an oily by-product consisting apparently of the *acetyl* derivative of the hydroxy-acid, as it was converted into the latter on hydrolysis with alkali). The new acid proved to be a liquid like its isomeride and had nearly the same boiling point (216°), but it was readily distinguished by the fact that it gave an *amide*, m. p. 89·5°, and a p-*toluidide*, m. p. 80·5°. Its constitution was established by oxidation with permanganate and with ozone (in the form of ester), when diethyl ketone was obtained. In accordance with the αβ-structure (V) assigned to them, both the acid and its ester showed an appreciable exaltation in their molecular refraction. A characteristic difference between the isomeric acids is found in the rate at which they absorb bromine; this also is in keeping with their constitution.

When the carefully purified αβ-acid was treated with boiling alkali for a short time, it was converted apparently completely into the βγ-isomeride. This doubtless accounts for the fact that, although Fichter, Kiefer, and Bernoulli must have actually obtained the ester of the αβ-acid from ethyl α-bromo-ββ-diethylpropionate and diethylaniline, $CHEt_2\cdot CHBr\cdot CO_2Et \longrightarrow CEt_2\colon CH\cdot CO_2Et$, the acid prepared by the hydrolysis of the ester with concentrated alkali was identical with that obtained by their first method, namely,

the βγ-acid. We have found that hydrolysis of the ester with even such a mild reagent as alcoholic sodium ethoxide leads to isomerisation. The αβ-acids are, in general, very sensitive to reagents, and the greatest care is necessary in order to obtain them free from their isomerides. It is for this reason that we did not adopt the method of Harding and Haworth (J., 1909, **95**, 1955), although their product must have consisted mainly of the αβ-acid, as it gave diethyl ketone on oxidation.

The simplest member of the series, ββ-dimethylacrylic acid, could scarcely be expected to undergo the αβ–βγ-change, because the relatively unstable terminal methylene group is known to be formed with difficulty and is sensitive to the action of even mild reagents. Numerous experiments were made on the dehydration of β-hydroxy*iso*valeric acid and its ester, with the object of obtaining the acid $CH_2:CMe \cdot CH_2 \cdot CO_2H$, but without success, and it was found that dimethylacrylic acid was quite unaffected by treatment with concentrated alkali. It may, however, be mentioned that the experiments of Bouveault and Wahl (*Compt. rend.*, 1900, **131**, 687), who prepared nitro-derivatives of the βγ- as well as of the αβ-form, point to the potential existence of the former.

It was all the more important for this reason to examine β-methyl-β-ethylacrylic acid (VIII) and its isomeride (IX), which, we found, could be readily prepared by the same general methods.

(VIII.) $\begin{matrix} Me \\ Et \end{matrix} \Big> C:CH \cdot CO_2H$ $\qquad\qquad \begin{matrix} Me \\ CHMe \end{matrix} \Big> C \cdot CH_2 \cdot CO_2H$ (IX.)
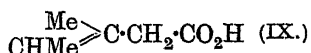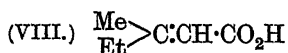
The αβ-acid was a solid, as described by Fichter and Gisiger (*Ber.*, 1908, **42**, 4707); it gave an *amide*, m. p. 92°, and a p-*toluidide*, m. p. 67°, and yielded methyl ethyl ketone and oxalic acid on oxidation with permanganate; the *ester*, prepared through the acid chloride, showed a marked exaltation of the molecular refraction. The βγ-acid was readily prepared by the usual method and also by boiling the hydroxy-acid with dilute sulphuric acid, although in the latter case a considerable amount of β-methylvalerolactone was formed as well. The acid, which could not be obtained solid at the ordinary temperature, was characterised by the formation of an *amide*, m. p. 123°, and a p-*toluidide*, m. p. 84°; by its oxidation to acetic acid; and by the formation of the ester, which, like the parent acid, showed a normal molecular refraction.

When the pure αβ-acid was treated with concentrated potassium hydroxide under the usual conditions, it underwent conversion to the βγ-acid, although the presence of a small quantity of unchanged acid is not excluded owing to the difficulty of detecting traces of this substance in the presence of its isomeride. There are at present

no trustworthy methods for the separation of such pairs of acids. Fittig's method fails completely, the αβ-acids of this series being converted into lactones like the βγ- (this was first observed by Fichter and his collaborators and confirmed by us, using materials of known purity). It can, however, be stated for the present that the methylethyl acids probably occupy a position intermediate between the diethyl and the dimethyl acids, the equilibrium being still very much on the side of the βγ-forms.

It is proposed in the near future to examine the effect of different substituent groups on the movement of the double bond, and to devise, if possible, more exact methods of estimating the relative stabilities of pairs of unsaturated acids.

EXPERIMENTAL.

Preparation of ββ-*Disubstituted Acrylic Acids and their* βγ-*Isomerides by the Reformatski Reaction.*

The method outlined below was found satisfactory in all the cases investigated.

The ketone * (0·75 g.-mol.), ethyl bromoacetate (84 c.c.), and benzene (300 c.c.) are heated with 22 g. of magnesium powder until the reaction begins, efficient cooling with ice-water being then necessary. The reaction product is finally heated for about 15 minutes, decomposed with ice and sulphuric acid, and the benzene solution, after shaking with dilute sulphuric acid, carefully washed with 10% sodium hydroxide. We find this precaution essential in order to obtain a pure and colourless product. The benzene solution is dried, the solvent removed under reduced pressure at as low a temperature as possible (to avoid risk of partial dehydration), and the ester purified by distillation under reduced pressure (yield 60—80%).

For the preparation of the αβ-acid, the hydroxy-ester is hydrolysed with alcoholic potassium hydroxide to the acid, which is then dehydrated with acetic anhydride (Wallach, *Annalen*, 1907, **353**, 288). The βγ-acids are best obtained by digesting the hydroxy-ester with potassium hydrogen sulphate (2 parts) for 3 hours at 160—180° and hydrolysing the resulting ester with alcoholic potassium hydroxide (Wallach, *Annalen*, 1902, **323**, 159).

cyclo*Pentane Series.*

cyclo*Pentanolacetic Acid.*—The acid prepared as above forms large flakes, m. p. 77° after crystallisation from benzene and light petroleum, and is anhydrous (Found : C = 58·41, 58·73; H = 8·33,

* It is advisable to use a 5 to 10% excess of ketone to ensure that all the ethyl bromoacetate is used up.

8·28. Calc., C = 58·29; H = 8·38%), whilst the acid prepared by Harding and Haworth (J., 1910, 97, 486) melted at 76° and is described as a semihydrate; it would appear probable, however, that their product contained some impurity.

*cyclo*Pentylideneacetic acid was obtained in about 60% yield and melted at 63—64°. Δ^1-*cyclo*Penteneacetic acid was prepared as described by Wallach (*Annalen*, 1906, 347, 324; 1902, 323, 1521), and melted at 51—52°; a mixture of the two acids melted a little above room temperature.

A solution of *cyclo*pentylideneacetic acid (3 g.) in 45 c.c. of 60% aqueous potassium hydroxide was boiled for 10 minutes. The acid, isolated in the usual manner and recrystallised from light petroleum (2·5 g., m. p. 51°; a further small quantity was recovered from the mother-liquor), was identified as Δ^1-*cyclo*penteneacetic acid by the method of mixed melting points; no trace of the original acid could be isolated from the reaction product.

Diethyl Series.

β-*Ethyl*-Δ^β-*pentenoic Acid* (VI).—The ester, b. p. about 95°/24 mm. or 187—188° at atmospheric pressure, was prepared by dehydrating ethyl β-hydroxy-ββ-diethylpropionate. The acid obtained by hydrolysing it with alcoholic potassium hydroxide had b. p. 133—134°/24 mm. or 217°/763 mm. and formed a colourless, fairly mobile liquid with a faint, disagreeable odour. This did not solidify when cooled to − 20°; it had $d_4^{22°7}$ 0·9727; $n_D^{22°7}$ 1·45073; $[R_L]_D$ 35·44 (calc., 35·60).

The *acid chloride*, b. p. 60—61°/14 mm., prepared by the action of thionyl chloride, was a colourless, mobile liquid.

The p-*toluidide*, prepared by the action of the base on the acid chloride or on the acid itself, crystallised from benzene and light petroleum in fine needles (compare Fichter, Kiefer, and Bernoulli, *loc. cit.*), m. p. 94°.

The *amide*, prepared from dry ammonia and the acid chloride in ethereal solution, crystallised well from acetone and light petroleum in plates, m. p. 113—114°, or from benzene and petroleum in needles (Found: C = 66·19; H = 10·19. $C_7H_{13}ON$ requires C = 66·12; H = 10·31%).

The *ethyl* ester, prepared from the pure acid chloride, boiled at 183°/755 mm. and had $d_4^{17°8}$ 0·9134, $n_D^{17°8}$ 1·43668, $[R_L]_D$ 44·75 (calc., 44·95). A chloroform solution of the pure ethyl ester was oxidised with ozonised oxygen; 3 g. required nearly 60 hours for complete oxidation. After removal of the solvent, the ozonide was decomposed with warm water in a current of carbon dioxide, the gases being led through a solution of β-naphthol in acetic acid containing

hydrochloric acid. The latter solution was then warmed for $\frac{1}{2}$ hour, cooled, and diluted, when the characteristic ethylidene-β-dinaphthyl oxide, m. p. 170—172°, separated, accompanied by the corresponding acetal, m. p. 200—201°; the yield of these two products, which were compared with specimens prepared from acetaldehyde, corresponded with an almost theoretical yield of acetaldehyde from the ozonide. The residue in the flask gave a deep red colour with alcoholic ferric chloride and presumably contained ethyl propionylacetate.

β-Ethyl-Δ^β-pentenoic acid readily absorbs two atoms of bromine in acetic acid solution to form an oily *dibromide* which could not be purified.

On boiling the acid with 50% (by volume) sulphuric acid for 15 minutes, a 60% yield of β-ethylvalerolactone, b. p. 226°, was obtained, although the yield was only 10% after 5 minutes.

ββ-*Diethylacrylic acid* (β-*ethyl-Δ^α-pentenoic acid*) was prepared from the corresponding hydroxy-acid in about 50% yield and boiled at 129°/23 mm. as a colourless liquid with a faint pungent smell; it had $d_4^{21\cdot2°}$ 0·9682, $n_D^{21\cdot2°}$ 1·46270, $[R_L]_D$ 36·42 (calc., 35·60) (Found : C = 65·30; H = 9·34. $C_7H_{12}O_2$ requires C = 65·59; H = 9·45%).

The *acid chloride* boiled at 85°/25 mm. The p-*toluidide* crystallised well from benzene and light petroleum, forming large needles, m. p. 80·5°; a mixture of this compound with the βγ-isomeride melted below 70° (Found : C = 77·31; H = 8·99. $C_{14}H_{19}ON$ requires C = 77·35; H = 8·81%).

The *amide* was much more soluble in acetone than its isomeride, but crystallised well from ether and light petroleum or benzene and light petroleum, forming long needles, m. p. 89° (Found : C = 66·33; H = 10·38. $C_7H_{13}ON$ requires C = 66·72; H = 10·31%).

The *ethyl* ester, prepared from the acid chloride, boiled at 87—88°/23 mm., 187—188°/755 mm., and had $d_4^{16\cdot6°}$ 0·90955, $n_D^{16\cdot6°}$ 1·44542, $[R_L]_D$ 45·72 (calc., 44·95) (Found : C = 68·60; H = 10·17. $C_9H_{16}O_2$ requires C = 69·18; H = 10·32%).

The pure acid was oxidised with alkaline potassium permanganate, and the product distilled in steam, when a quantity of diethyl ketone was obtained (identified as the semicarbazone, m. p. 135°); the residue in the flask contained oxalic acid. The same products were also obtained by oxidising the ester with ozone; the oxidation was much slower and less complete than in the case of the isomeric acid. The αβ-acid reacted very incompletely with bromine, only about 25% of the theoretical amount being absorbed in the cold. A solid bromide could not be isolated.

The action of sulphuric acid on the αβ-acid, on the other hand, proceeded exactly as in the case of the βγ-acid, a yield of about 60% of the same lactone being produced in 15 minutes.

βγ-*Diethylacrylic acid* was treated with 60% potassium hydroxide exactly as described in the case of *cyclo*pentylideneacetic acid (p. 621), the mixture being allowed to boil for 20 minutes. The acid isolated had $d_4^{21\cdot7^\circ}$ 0·9629, $n_D^{21\cdot7^\circ}$ 1·45223, $[R_L]_D$ 35·90, thus showing that a considerable amount of conversion to the βγ-isomeride had taken place. It was then converted through the acid chloride into the amide, which melted at 107° after one crystallisation; no trace of the isomeric amide, m. p. 89°, could be isolated. The experiment was repeated, starting with the pure βγ-acid; the product showed $d_4^{19\cdot1^\circ}$ 0·9644, $n_D^{19\cdot1^\circ}$ 1·45183, $[R_L]_D$ 35·82 and the amide prepared from it melted at 114° after one crystallisation. It follows, therefore, that the point of equilibrium is very much on the side of the βγ-acid.

Methylethyl Series.

β-*Methyl-Δβ-pentenoic Acid* (IX).—This acid, b. p. 116°/23 mm., was prepared by the standard method or by dehydrating the hydroxy-acid with 12% sulphuric acid. When anhydrous formic acid was used in place of sulphuric acid as dehydrating agent, the product contained about 30% of the isomeric αβ-acid. The acid had $d_4^{23\cdot2^\circ}$ 0·97845, $n_D^{23\cdot2^\circ}$ 1·44692, $[R_L]_D$ 31·15 (calc., 30·98).

The *acid chloride* boiled at 57°/25 mm. The p-*toluidide* crystallised from light petroleum containing a little benzene in fine needles, m. p. 84° (Found: C = 76·70; H = 8·49. $C_{13}H_{17}ON$ requires C = 76·79; H = 8·43%). The *amide* separated from benzene and light petroleum in silvery plates, m. p. 123—124°. The *ethyl* ester boiled at 62°/13 mm. and had $d_4^{18\cdot8^\circ}$ 0·91633, $n_D^{18\cdot8^\circ}$ 1·43638, $[R_L]_D$ 40·58 (calc., 40·33).

The acid was oxidised with alkaline potassium permanganate, when acetic acid was isolated; no trace of oxalic acid was produced. The ester was oxidised with ozone and the ozonide decomposed with water, a good yield of acetaldehyde being obtained.

β-*Methyl-β-ethylacrylic Acid* (β-*methyl-Δα-pentenoic acid*).—This acid was produced in 34% yield from the hydroxy-acid; it boiled at 121—122°/22 mm., solidified on cooling, and formed flattened needles, m. p. 45°, when recrystallised from light petroleum.

The *acid chloride* boiled at 65°/25 mm. The p-*toluidide* formed needles from benzene and light petroleum or plates from ether and light petroleum, m. p. 66—67°; a mixture of this substance with its isomeride, m. p. 84°, melted at about 52° (Found: C = 77·09; H = 8·53. $C_{13}H_{17}ON$ requires C = 76·79; H = 8·43%). The *amide* crystallised from benzene and light petroleum in plates,

m. p. 92—93°; a mixture of this compound with the βγ-isomeride melted at about 70° (Found: C = 64·04; H = 9·71. $C_6H_{11}ON$ requires C = 63·60; H = 9·78%). The *ethyl* ester boiled at 67°/24 mm. and had $d_4^{17\cdot9°}$ 0·91413, $n_D^{17\cdot9°}$ 1·44110, $[R_L]_D$ 41·06 (calc., 40·33).

Both the acid and the ester were oxidised and gave methyl ethyl ketone (*p*-nitrophenylhydrazone, m. p. 126°) and oxalic acid.

The acid was treated with potassium hydroxide under the same conditions as the diethyl acid (p. 621). The acid isolated was a liquid, b. p. 113—115°/23 mm., $d_4^{23\cdot1°}$ 0·97772, $n_D^{23\cdot1°}$ 1·44753, $[R_L]_D$ 31·21; the amide prepared from it melted at 119—120° in the crude state and at 123—124° after one crystallisation. In another experiment the acid after treatment with potassium hydroxide was characterised by means of the p-*toluidide*, which melted at 84° after one crystallisation. The βγ-acid was treated with alkali in the same way. The product gave an amide melting in the crude state at 90—95°, at 117° after one crystallisation. The amount of conversion to the αβ-acid was therefore very small, but possibly somewhat greater than in the case of the higher homologue.

Dimethyl Series.

The condensation of acetone with ethyl bromoacetate in benzene solution in presence of magnesium does not proceed easily, there being an " induction period " of about 3 days; once started, the reaction is very vigorous. The hydroxy-ester, b. p. 88—89°/19 mm., is obtained in a yield of about 40%. All the methods of dehydrating the hydroxy-ester or the acid led to ββ-dimethylacrylic acid, which was identified in the usual way. This acid was quite unaffected by boiling with 60% aqueous potassium hydroxide for ½ hour.

XCI.—*A Method of Determining the Presence or Absence of Complex Salts or Ions in Dilute Aqueous Solution.*

By WILLIAM HAMILTON PATTERSON and JOHN DUCKETT.

THE temperature of mutual miscibility of two liquids is in general markedly altered by the addition of even small quantities of other components.

The following experiments were carried out with phenol (36·1%) and water (63·9%), proportions which, even with slight variation, give the critical solution temperature of 66·0° (temperature of critical turbidity). The added substances were inorganic salts, or mixtures of two salts, the object in the latter case being to test whether or not the two existed independently in solution.

Symbols similar to those of Timmermans (*Z. physikal. Chem.*, 1907, **58**, 129) have been adopted : C = concentration of salt per 1000 g. of total solution (phenol + water + salt). Mol. C = molecular concentration. e = elevation of critical solution temperature. E = molecular elevation = e/mol. C.

From the values of E or e conclusions can be drawn as to the condition of the salts in dilute aqueous solution, in this case above 66° (when the proportions of phenol and water given above are used).

These conclusions are based on the following observations — The simpler inorganic salts are soluble in the aqueous phase only and therefore greatly raise the critical solution temperature. In a previous communication (*J. Physical Chem.*) we have shown that the increase of critical solution temperature caused by the addition of various salts is the sum of the ionic values, and that the anions and kations may be arranged, in this respect, in a series almost identical with the Hofmeister series (for the coagulation of neutral egg-albumin).

Further, valency has a great effect on the critical solution temperature, the substitution of a bivalent for a univalent ion producing a much greater increase than that of a tervalent for a bivalent ion. Hence the more complex the molecule the greater the rise obtained on dissolving equimolecular quantities; *e.g.*, the addition of 0·03 mol. of the salts named gives the following values of e : KCl 2·95°, NaCl 3·75°, K_2SO_4 7·95°, Na_2SO_4 9·7°, $MgSO_4$ 10·75°, $Cr_2(SO_4)_3$ 15·0°.

Curves showing the relation between e, or E, and mol. C have been plotted for a number of salts. The former curves (see Fig. 1), after an initial bend at low concentration, approach a straight line, so that intra- or even extra-polation can be made within the limits of experimental error (temperatures being measured to 0·05°).

For salt pairs, additive values of e imply that neither complexes nor double molecules exist in the solution. Deviations from the separately calculated values measure the molecular complexity.

Simple Mixtures.

Lithium chloride, mol. C 0·1141, + *potassium chloride*, mol. C 0·1131. e (observed for mixture) 18·6°.

In this, and every other case, the rise calculated from the values for the components agrees best with that found experimentally (for the mixture) when the mean for the double concentration of each separately is chosen : e.g., e for 0·2282 mol. C of LiCl (from the curve) = 19·75°, and for 0·2263 mol. C of KCl, 17·50°; mean 18·63°. Simply to add together the values of e for each salt is to ignore the presence of the other salt already in solution and results in a slight deviation from the experimental value. The above method of calculation has therefore been adopted throughout.

Fig. 1.
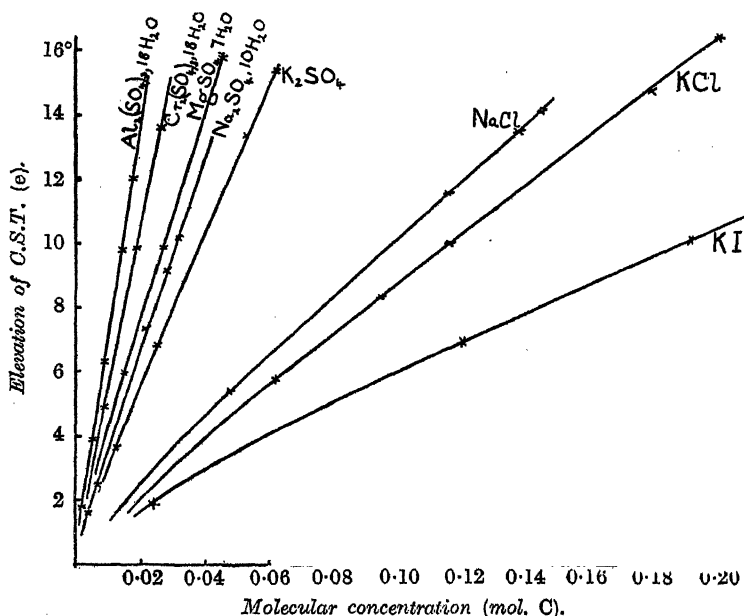
Sodium chloride, mol. C 0·1047, + potassium chloride, mol. C 0·1047.

The calculated and the experimental value of e agree, 18·4°.

This result, provided the temperature difference affords no explanation, is not in harmony with the theory of Braley and Hall (J. Amer. Chem. Soc., 1920, 42, 1770), who account for the transference numbers of sodium and potassium in mixed chloride solutions at 25° by postulating the existence of complexes,

$$NaCl + KCl \rightleftharpoons Na(KCl_2) \rightleftharpoons Na^{\cdot} + KCl_2';$$
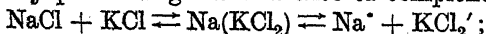
an argument made use of in favour of progressive ionisation of strong electrolytes with increasing dilution.

$MgSO_4 + KCl.$

	Mol. C.	e calc.	Mean calc.	e obs.
$MgSO_4$	0·0211	14·51° }	9·3°	9·9°
KCl	,,	4·03 }		
$MgSO_4$	0·0324	21·7 }	13·8	13·9
KCl	,,	5·92 }		

$K_2SO_4 + MgSO_4.$

	Mol. C.	e calc.	Mean calc.	obs.
K_2SO_4	0·0138	7·38° }	8·7°	8·75°
$MgSO_4$	,,	9·98 }		
K_2SO_4	0·0293	14·23 }	16·9	17·8
$MgSO_4$	,,	19·61 }		

$Na_2SO_4 + MgSO_4.$

	Mol. C.	e calc.	Mean calc.	e obs.		Mol. C.	e calc.	Mean calc.	obs.
Na_2SO_4	0·00666	4·42° }	5·0°	5·7°	Na_2SO_4	0·0166	10·42° }	11·0°	10·7°
$MgSO_4$	,,	5·50 }			O_4	,,	11·61 }		
Na_2SO_4	0·01045	6·90 }	7·4	7·7	Na_2SO_4	0·0218	13·6	14·2	14·2
$MgSO_4$	,,	7·95 }			$MgSO_4$	,,	14·9		

Potassium alum.

Mol. C. (as double mol.). $\times 10^3$	e calc. for double C of each salt component. $K_2SO_4.$	$Al_2(SO_4)_3.$	e calc. Mean.	e obs.
3·49	2·1°	4·8°	3·5°	3·8°
7·63	4·43	10·1	8·4	8·2
17·63	5·1	11·6	11·9	11·8
18·26	9·25	24·2	16·7	15·4
22·75	11·2	30·0	20·6	19·0

Chrome alum.

Mol. C. (as double mol.). $\times 10^3$	e calc. for double C of each salt component. $K_2SO_4.$	$Cr_2(SO_4)_3.$	e calc. Mean.	e obs.
2·2	1·5°	2·8°	2·2°	2·2ᶜ
7·1	4·15	7·3	5·8	5·8
16·0	8·40	15·62	12·0	11·6
24·7	12·1	23·4	17·8	17·2

Iron Alum.—The curve for iron alum lies just below that of potassium alum, and the result, by analogy, may be taken as similar.

The small deviation for the higher concentrations in the case of potassium alum may imply a tendency to form double molecules (the ordinary alum molecule) with increasing concentration, in spite of the higher temperature; the number formed, however, must be relatively small.

A series of separate experiments up to 47·5° with a phenol–water mixture having a temperature of mutual miscibility 34·8° indicated appreciable formation of the alum molecule. Errors due to hydrolysis of aluminium sulphate, chemical reaction with phenol, etc., may be expected to compensate in the case of simple mixture.

Complex Formation.

The trustworthiness of the method was tested by selecting cases where complex formation might be expected to occur.

Sodium Ferrocyanide.—The curve (plotted for the normal molecular weight) lies just above that of aluminium sulphate. The following figures are normal and indicate no change of condition of the salt in solution.

C	Mol. C.	C.S.T.	e.	E.
2·682	0·0055	70·75°	4·75°	857°
4·220	0·0087	72·9	6·9	791
5·765	0·0119	74·85	8·85	743
7·913	0·0164	77·8	11·8	722

Y ;

Sodium cyanide, mol. C 0·0094—0·0224, produces the largest lowering of critical solution temperature found for any substance, E — 1559 to — 1192. The curve bends, indicating probably the extent of hydrolysis.

Sodium Ferrioxalate.—The curve is nearly identical with that of chromic sulphate. Mol. C 0·0152—0·036. $E = 552$—493. Sodium oxalate, mol. C 0·066—0·093. $E = 273$—210.

Even in saturated sodium sulphate solution, both sodium ferrocyanide and sodium ferrioxalate must be strongly ionised (compare Turner and Patterson, *Trans. Faraday Soc.*, 1924, **20**, 345); a part of the ions must therefore be complex.

Mercuric Iodide + Potassium Iodide.—

	Mol. C.	e.	E.	
HgI_2	0·0043	0·2°	46·6°	(limit of solubility)
KI	0·0250	1·85	74·0	
	0·1215	6·95	57·7	
	0·193	10·15	52·7	
	0·347	17·1	49·4	
Equimolecular mixture	0·0616 of each	—9·1	—74	

These results indicate combination between the molecules and also that the complex is appreciably soluble in phenol.

Cadmium Iodide.—Mol. C 0·0106. $e = 0·7°$. The value of e remains the same as mol. C increases to 0·049; this can only be due to increasing complexity. The value for Cd˙˙ (ion) obtained from cadmium chloride or sulphate is normal; Cd = 2 Na (approx.).

Cadmium Iodide + Potassium Iodide.—On adding a molecular equivalent of potassium iodide to cadmium iodide, e became 1·10°, a rise of only 0·4°, instead of the 3·4° to be expected if only simple mixture had occurred. Complex formation may thus be supposed to occur to the extent denoted by the ratio $(3·4—0·4)/3·4$.

In conclusion, the authors desire to express their thanks to Messrs. J. H. Carrington and L. R. Hickson for making the experiments with lithium chloride and for repeating several of the determinations.

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XCII.—*Studies on Starch. Part II. The Constitution of Polymerised Amylose, Amylopectin, and their Derivatives.*

By ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI.

A CONTINUATION of our experiments (J., 1923, **123**, 2666) has led to results which have enabled us to draw definite conclusions on the subject as well as to reconcile our work with that of others.

Some misconception has arisen with regard to the quantity of amylose and amylopectin in starch granules. Thus Samec and Höft (*Koll. Chem. Beihefte*, 1913, **5**, 141) assert that starch contains 17% of " amylose " and 83% of amylopectin. Pringsheim and Wolfsohn (*Ber.*, 1924, **57**, [B], 887), who prepared " amylose " by one of our methods (*loc. cit.*, p. 2673), were able to obtain only 14% from anhydrous starch. They therefore accept the views of Samec and Höft, in spite of the fact that they were not able to obtain more than 28% of amylopectin from starch. We shall show that in those starches which contain " amylose " and amylopectin only, these substances are present to the extent of 66·6 and 33·3%, respectively. The explanation of the discrepancies is that " amylose " as it exists in starch granules is present in more than one physical state and possibly in different degrees of hydration. From an histological investigation of starch granules, an account of which will be published elsewhere, we find that about 25% of the " amylose " exists as a crystalloidal phase in the form of spherites constituting a core round the hilum of the granule. This portion is readily extracted by water or by dilute alkali. The remainder, which presents a colloidal phase, is dispersed uniformly in the amylopectin layers. It appears to exist either as a solid solution or to be so strongly adsorbed on the amylopectin as to resist extraction. It is, however, quite possible to remove the whole of the amylose from starch paste by treating the latter with barley diastase at 50°, whereby the amylose is converted into maltose and the amylopectin into αβ-hexa-amylose. Ling, Nanji, and Harper (*J. Inst. Brewing*, 1924, **30**, 838) have utilised these facts in a method of estimating " amylose " and amylopectin in barley and wheat.

When a solution of amylose is treated with a minute quantity of barley or malt diastase at p_H 4·5, it is converted rapidly into maltose, the optimum temperature being between 30° and 40° for the former and 45° for the latter. At 70°, scarcely any action occurs. No intermediate sugar is formed as in the case of αβ-hexa-amylose.

Since Neuberg and Saneyoshi (*Biochem. Z.*, 1911, **34**, 44; *Z. Ver.*

deut. Zuckerind., 1912, 559) have shown that the osazones of the bioses are capable of being hydrolysed by enzymes, this afforded a means of establishing the constitution of the trihexose derived from amylopectin which, as previously stated (*loc. cit.*), may be either β-glucosidomaltose or α-glucosido*iso*maltose. To decide between these alternatives, we have studied the products of hydrolysis of the osazone of the trihexose by the α- and β-enzymes, maltase and emulsin. We find that under the action of maltase at 38° the products are glucosazone and *iso*maltose, whilst under the action of emulsin at 38° they are maltosazone and glucose. Consequently the trihexose is β-glucosidomaltose,* $C_6H_{11}O_5 \cdot O \cdot \underset{\beta}{C_6H_{10}O_4} \cdot O \cdot \underset{\alpha}{C_6H_{10}O_5}$.

The structure previously assigned to αβ-hexa-amylose, which is shown in skeletal form in (I), demands the production of two tri-

hexoses, *viz*, β-glucosidomaltose and α-glucosido*iso*maltose, whereas the product obtained by the action of malt diastase at 70° on amylopectin and consequently on αβ-hexa-amylose consists, as shown above, exclusively of β-glucosidomaltose. The structure I requires therefore some modification to accommodate this fact. If one of the trihexose halves in the αβ-hexa-amylose, *viz*., that representing α-glucosido*iso*maltose, be turned through 180°, a structure is obtained which can yield on hydrolysis entirely β-gluco-
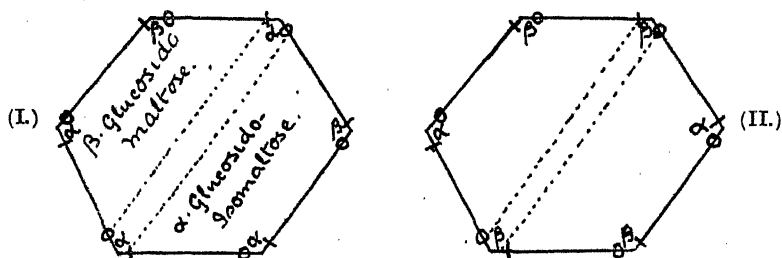
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* In Part I, the constitution of the *iso*maltose unit was provisionally put forward as 1 : 5-glucosidoglucose. The precise constitution of this disaccharide is at present *sub judice*, and this together with Haworth's observation, that cellobiose is 1 : 5-glucosidoglucose, leads us to the view that the precise constitution of *iso*maltose should be left open for the present. This much, however, we may state. The β-linkings used throughout the papers to represent the *iso*maltose unit may either be 1 : 5 or 1 : 4, and the oxidic ring, butylene- or amylene-oxide respectively. Both these alternatives account for the production of 2 : 3 : 6-trimethyl glucose from starch (Irvine and Macdonald, J., 1924, 125, 942). Even if 2 : 3 : 6-trimethyl glucose is not obtained from isolated *iso*maltose, the possibility is not excluded that there may be a shifting of the amylene-oxide ring in αβ-hexa-amylose on its hydrolysis with enzymes or acids to a hexylene-oxide ring, just as in the hydrolysis of sucrose an amylene-oxide ring passes into a butylene-oxide ring (Haworth and co-workers, J., 1923, 123, 294).

sidomaltose. But the linkings of the two β-glucosidomaltose units present three possibilities. They may be both α-linkings, one may be an α- and the other a β-linking, or both may be β-linkings. When we come to consider the nature of the so-called stable dextrin (see Part III), it will be seen that preference must be given to formula (II) as representing the constitution of αβ-hexa-amylose.

Throughout the work the exploring agents employed were exclusively enzymes, and by their aid we have not only realised quantitative yields of hydrolytic products, but have been able to assure ourselves that no secondary changes occurred. It seems, therefore, at first sight surprising that our conclusions should conflict with those of Irvine, Pringsheim, and Macdonald (J., 1924, 125, 942) on the molecular structure of αβ-hexa-amylose. The differences in our views would seem, however, to be apparent rather than real. But there are fundamental differences in the way in which the problem has been attacked by the chemists just mentioned and by ourselves. In the first place, Irvine, Pringsheim, and Macdonald worked on β-hexa-amylose obtained from one of the products of the action of *Bacillus macerans* on starch. As the parent substances thus formed—the crystalline " dextrins " of Schardinger—are products of the metabolism of an organism, their relation to the constituents of starch itself is uncertain. In any event they do not exist as such among the integral constituents of starch granules. Secondly, the chemical treatment, methylation, to which the β-hexa-amylose was subjected is open to criticism, as there is reason to believe from the evidence furnished by the authors themselves that secondary changes occurred, whilst the yield of trimethyl-amylose was only 29% of the theoretical. Its product of hydrolysis was 2 : 3 : 6-trimethyl glucose, a fact which may indicate its relation to our αβ-hexa-amylose. Indeed, in our previous paper (*loc. cit.*, p. 2669), we put forward the view that Pringsheim's β-series of amyloses belongs to the same series as our αβ-hexa-amylose. That being so, the absence of 2 : 3 : 5-trimethyl glucose at which Irvine, Pringsheim, and Macdonald express surprise must be due, as previously suggested, to steric hindrance. The major portion of the product obtained by the methylation of β-hexa-amylose consisted (apart from substances due to secondary changes) of derivatives, the methoxyl content of which was below that required for a trimethylamylose.*

* In a footnote to the paper by Irvine, Pringsheim, and Macdonald (*loc. cit.*, p. 943) it is stated that opportunity is taken to *correct* certain statements made by us in the previous paper that " *in establishing the constitution of such closed-chain compounds (amylose) a very important factor presents itself which has been left out of consideration, namely, that of steric hindrance.*" None of

EXPERIMENTAL.

Hydrolysis of α-Hexa-amylose with the Diastase from Malt and Barley.

Velocity of Hydrolysis of "Amylose" with Malt Diastase at Different Temperatures.—Four 100 c.c. portions of a 1% solution of amylose brought to p_H 4·5 were treated at 30°, 40°, 50°, and 70° with a solution containing 2 mg. of precipitated malt diastase, and these portions were kept at the respective temperature for 5 minutes, the reaction being then arrested by the addition of a drop of 10% caustic soda solution. The liquids were then made up to 200 c.c. and titrated against 5 c.c. of Fehling's solution. The results are shown in the following table (a = percentage of amylose hydrolysed in 5 minutes), from which it will be seen that the optimum temperature lies between 30° and 40°.

Temp.	30°	40°	50°	70°
a.	97·2	98·7	78·3	15·1
Iodine coloration	nil	nil	very feeble	deep blue

The remaining portions of the solutions representing the conversions carried out at 30° and 40° were combined and concentrated to a small volume. The dissolved matter was completely fermentable with yeast and gave maltosazone. The sugar was therefore maltose.

Hydrolysis of α-Hexa-amylose at 70° with Malt Diastase Previously Heated to the Same Temperature.—Malt diastase solution which had been previously heated at 70° for ½ hour was practically without action on "amylose" even after incubating at 70° for 2 hours. With malt-diastase solution previously heated for a shorter period

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the fresh arguments brought forward by the authors contradicts our statement and therefore we fail to see the necessity for any "correction."

We must still maintain that the conception of steric hindrance and its connexion with carbon atom 5 have never been alluded to directly in any paper dealing with constitutional studies on the *polysaccharides* published prior to our paper. We may ask the question—If the effect of steric hindrance at position 5 were so well known, why was the presence of 2 : 3 : 5-trimethyl glucose vainly sought for among the products of hydrolysis of methylated starch, and why were all those considerations which involved the formation of this trimethyl glucose finally rejected? To quote Irvine's words at the meeting of the British Association (1922)—when he rejected Karrer's formula for his diamylose on exactly the above grounds—" *The only trimethyl glucose to which such a structure could give rise is the 2 : 3 : 5-form described by Irvine and Oldham*" (J., 1921, **119**, 1744). He proceeds: "*No trace of this compound was detected by us, and moreover the 2 : 3 : 6-variety of trimethyl glucose actually obtained cannot possibly be accommodated by Karrer's formula.*" In the light of our own work the 2 : 3 : 6-variety must therefore have been obtained from the amylopectin portion of the rice starch employed by Irvine, which cannot be regarded as a chemical entity, containing as it does three distinct substances.

at 70°, the percentage of amylose hydrolysed was exceedingly low.
The sugar formed under these conditions was identified as maltose.

*Velocity of Hydrolysis of α-Hexa-amylose with Barley Diastase at
Different Temperatures.*—Four 100 c.c. portions of a 1% solution
of the " amylose " at p_H 4·5 were raised to 30°, 40°, 45°, and 50°,
respectively, and treated at these temperatures for 5 minutes with
2 c.c. of barley diastase solution (equivalent to 2 g. of barley).
The reducing powers were then determined as in the case of the
similar experiments with malt diastase.   The results are as follows :

Temp..............................	30°	40°	45°	50°
% Maltose produced	38·0	44·9	55·3	53·2
% " Amylose " hydrolysed ...	36·0	42·5	52·4	50·4

A 2% solution of the amylose (100 c.c.) was treated with 5 c.c. of
a solution of barley diastase (equivalent to 5 g. of barley) for 3 hours,
when it no longer gave a coloration with iodine.   The constants
of the solution were $[\alpha]_D$ 137·8° and R 98·7, substantially those of
maltose, and it was proved to consist exclusively of maltose.

*Relative Quantities of α-Hexa-amylose and of αβ-Hexa-amylose in
Different Starches.*

When a starch paste is treated with barley diastase at a convenient
temperature, say 50°, the " amylose," being completely converted
into maltose, may be measured by the reducing power.   The
percentage of maltose thus formed may be converted into amylose
by the factor 0·947, the percentage of amylopectin being the difference
between 100 and the percentage of " amylose."   The results of the
estimation of " amylose " and amylopectin in different starches are
given below.

Starches.	Percentage of " Amylose."	Percentage of Amylopectin.
Arrowroot	65·8	34·2
Potato	67·2	32·8
Wheat	66·3	33·7
Barley	68·2	31·8
Rice	66·2	33·8

It should be pointed out that the values given in the table for the
percentages of " amylose " and amylopectin in the case of the
starches of barley, wheat, and rice are only relative, and that
the actual percentages of " amylose " and amylopectin calculated
on these starches would be considerably lower depending on their
hemicellulose content, which may vary between 8 and 18%, or in
some cases, maize for example, it may be less.   In these starches
a part of the hemicellulose is intimately associated with the granules,
forming, in fact, an integral portion of them, and therefore it cannot
be separated by any physical means.   The other portion of the

Y*

hemicellulose is derived from the cell wall and it is present to a greater or less extent according to the degree of fractionation to which the starch has been subjected in its manufacture. When a paste from any of the starches is treated with barley diastase at about the optimum temperature, the " amylose " is, as we have seen, converted into maltose, the amylopectin is dephosphated and depolymerised, whilst the hemicellulose is left unaltered and may be filtered off from the soluble products.

It may be pointed out that, provided the barley diastase is freshly prepared from a barley which is sound and has undergone no modification during harvesting or storage, no abnormalities in its chemical activity need be feared.

Hydrolysis of the Trihexosazone with Maltase.—A solution of the osazone (0·8 g.) in hot water was cooled to 38° and a cold water extract of dried yeast corresponding with about 3 g. of the yeast added. After the addition of a little toluene the mixture was incubated at 38° for 96 hours, within which time the hydrolysis was practically complete. After about 48 hours, the liquid became cloudy and subsequently turbid. Finally, when the liquid was cooled in an ice-chest, a precipitate separated which was identified as glucosazone by its crystalline form and melting point (201°). Since part of the osazone remained dissolved, it was not possible to estimate the yield.

The filtrate from the glucosazone was acidified with a few drops of acetic acid and heated with a small quantity of norit, which removed the glucosazone. The liquid without filtering was made up to 100 c.c. and filtered. The reducing power of the filtrate was equal to 0·31 g. of maltose or 0·38 g. of *iso*maltose per 100 c.c. Theoretically 0·8 g. of the triosazone should yield 0·4 g. of a disaccharide.

The portion of the filtrate remaining after the determination of the reducing power was divided into two parts. One part was concentrated on a water-bath to a small volume and heated with phenylhydrazine acetate in the usual manner. The osazone which separated after about 12 hours was *iso*maltosazone; it melted at 145°. Twenty-five c.c. of the filtrate were incubated with emulsin in presence of a little toluene for 24 hours, a blank experiment with emulsin being carried out under the same conditions. The solution was then diluted to 50 c.c., and its reducing power determined; the latter corresponded with 0·32 g. of *iso*maltose per 100 c.c. instead of 0·19 g., the value before the action of the emulsin.

Hydrolysis of the Trihexosazone with Emulsin.—A solution of 0·8 g. of the osazone in hot water was cooled to 38° and incubated at that temperature with a solution of emulsin corresponding

with 5 g. of bitter almonds in presence of a little toluene for 96 hours.

Slight resinification occurred during the incubation unless air was excluded. To overcome this difficulty, a narrow-necked flask was filled to the neck with the solution, the surface of which was then covered with a layer of toluene, and the flask closed with a cork. After being incubated for 96 hours at 38°, the osazone solution showed no turbidity. After keeping at the room temperature for about 12 hours, a small quantity of minute, yellow crystals having the characteristic appearance under the microscope of maltosazone separated; m. p. 188° (maltosazone when not quite pure melts at about this temperature). The quantity obtained was not sufficient for recrystallisation, but we have no doubt whatever that the substance was maltosazone. The filtrate was acidified with a few drops of acetic acid and gently warmed with a little norit. It was cooled and made up to 100 c.c.; the reducing power of the filtrate corresponded with 0·19 g. of glucose per 100 c.c. instead of 0·22 g., the theoretical quantity. The remainder of the filtrate was concentrated to a small volume and heated with phenylhydrazine acetate in the usual manner. After a short time, a yellow, crystalline precipitate separated which was identified as glucosazone by its crystalline form and melting point.

Comparative Velocity of Hydrolysis of α- and β-Linkings.—To investigate this point, maltase and emulsin were allowed to act on maltose, and on *iso*maltose and the trihexose.

Experiments with maltase. Two solutions were prepared, one containing 2 g. of anhydrous maltose, and the other 3 g. of β-glucosidomaltose. To each was added the same quantity of a solution containing yeast maltase. Both solutions were then made up to 200 c.c. and after the addition of a trace of toluene they were incubated at 38°, portions being withdrawn at different intervals and the reducing powers determined. From the increase in the reducing powers, the percentage of α-linking hydrolysed could be calculated.

Experiments with emulsin. These experiments were carried out on the same lines as those in which maltase was used, but the substrates were *iso*maltose and β-glucosidomaltose.

The results of both series are given in the following table :

Substrate.	Maltose.	β-Glucosido-maltose.	*iso*Maltose.	β-Glucosido-maltose.
Time (hrs.).	% of α-linking hydrolysed.	% of α-linking hydrolysed.	% of β-linking hydrolysed.	% of β-linking hydrolysed.
1	32·6	30·1	28·2	24·6
2	58·1	55·8	52·5	45·0
4	72·3	68·7	65·8	57·9
6	82·5	76·4	75·1	66·4
24	99·2	93·6	98·6	92·0

It is seen from these results that whilst there is no essential difference in the action of the two enzymes on maltose, *iso*maltose, and the trihexose, the velocity of hydrolysis is sensibly greater in the case of the two bioses than in that of the triose.

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XCIII.—*Studies on Starch.   Part III.   The Nature and the Genesis of the Stable Dextrin and of the Maltodextrins.*

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IT has been shown (preceding paper) that α-hexa-amylose is converted quantitatively into maltose by barley or malt diastase at 50° without the production of any intermediate substances, whereas αβ-hexa-amylose under the action of malt diastase at 70° yields β-glucosidomaltose, *iso*maltose, maltose, and glucose according to the conditions.   We shall now show that αβ-hexa-amylose, when treated with malt diastase between 30° and 70° in presence and in absence of maltose, gives rise to a series of products intermediate between it and the β-glucosidomaltose.

We apply the term maltodextrin to all those non-crystalline, intermediate products of the action of diastase on starch possessing cupric-reducing power, with the exception of β-glucosidomaltose and *iso*maltose, which we regard as sugars, because they yield well-defined phenylosazones.   The well-known fact that when potato starch or a solution of soluble starch is hydrolysed with malt diastase, maltose and a series of maltodextrins are produced, seems at first to stand in conflict with the results previously described on the hydrolysis of amylopectin or αβ-hexa-amylose.   We have observed, in the course of an extended study of the kinetics of the different products of hydrolysis of starch, that amylopectin and its derivatives, αβ-hexa-amylose, and the maltodextrins (including the stable dextrin) exhibit marked differences when they are submitted to hydrolysis with malt diastase in presence or in absence of maltose.   Further, a variety of factors such as mass of diastase relative to

that of the substances undergoing change, temperature, etc., are of influence in determining the nature of the products.

It is a general rule in reactions brought about in presence of enzymes that, as the products of change accumulate, the velocity of the reaction slackens. In many cases the phenomenon is so marked that the reaction in its final stages no longer obeys an ordinary single law of mass action. The several hypotheses adduced in explanation of this phenomenon may be summarised as follows : First, it may be due to the reduction of concentration of the substrate; secondly, it may arise from the retarding action of the products of the reaction as they accumulate; and thirdly, in the case of a substrate such as starch paste, it is conceivable that one constituent is hydrolysed more rapidly than the others according to the conditions of the experiment. The second and third hypotheses taken together furnish, in the light of our experiments, an explanation of the difference in the products formed from starch as a whole and from amylopectin, respectively, when these are submitted to the action of malt diastase.

Wohl and Glimm (*Biochem. Z.*, 1910, **27**, 349) have shown that the presence of maltose retards the complete hydrolysis of starch. We find that when a mixture of 1 part of $\alpha\beta$-hexa-amylose and 2 parts of maltose—the proportions obtained from starch by the action of diastase from ungerminated barley at 50°—is submitted to the action of malt diastase at 55°, the reaction soon slackens, just as it does in the case of starch paste or of soluble starch solution. At this point the percentage of apparent maltose * deduced from the cupric-reducing power amounts to 78—80% of the total dissolved solids, and the specific rotatory power is $[\alpha]_D$ 146·5—147°. Moreover, these values remain constant when the incubation period is extended to 3 hours. The constants are substantially those of equation 8 of Brown and Heron (J., 1879, **35**, 647) and it will be remembered that Brown and Morris (J., 1885, **47**, 543) and Brown and Millar (J., 1899, **75**, 315) separated from starch degraded to this stage a substance which they designated " stable dextrin." This substance, of the existence of which as an actual chemical entity there is some doubt, we regard as a maltodextrin of the highest type.

The early history of the maltodextrins is well known (see Herzfeld, *Bied. Zentr.*, 1880, 347 ; Brown and Morris, *loc. cit.* ; Brown and Millar, *loc. cit.*). The last-named give the constants of maltodextrins as $[\alpha]_D$ 181—183° and R 42—43. Maltodextrin is a non-crystalline

* The percentage of apparent maltose produced depends to some extent on the diastatic power of the enzyme employed. In the case of malts or of diastase preparations which are very active the percentage of apparent maltose may be much higher (see Ling, *J. Inst. Brewing*, 1922, **28**, 838).

substance and according to Brown and his colleague it is unferment-
able by *Saccharomyces cerevisiæ*, and completely converted into
maltose by malt diastase. Two members of the maltodextrin
series were isolated and examined by Ling and Baker (J., 1895,
67, 703; 1897, 71, 517). They describe them as maltodextrin-α
and -β, respectively. The α-substance has the formula $C_{36}H_{62}O_{31}$ and
the constants $[\alpha]_D$ 180° and R 32·8, whilst the β-substance has the
formula $C_{24}H_{42}O_{21}$ and the constants $[\alpha]_D$ 171·6° and R 43.

We may state that as a result of a thorough examination of the
products of hydrolysis of starch under diverse conditions, we are
led to conclude that only three distinct types of maltodextrin exist,
namely, stable dextrin, maltodextrin-α, and maltodextrin-β. Mak-
ing use of the constants published by Ling and Baker, it is possible
to assign to the substances their position in the series and their
respective constitutions. On the other hand, we felt that the
properties of the stable dextrin and its method of isolation as
previously described needed some revision.

We find that when $\alpha\beta$-hexa-amylose is hydrolysed with malt
diastase in absence of maltose it yields one part of maltose and two
parts of *iso*maltose, whilst in presence of maltose it yields a mixture
of maltose and *iso*maltose, the relative quantities of which are
governed by several factors such as temperature, quantity of
diastase, etc., but the limit in this case is two parts of maltose and
one part of *iso*maltose. Further, it seems that when amylopectin
is hydrolysed by malt diastase in presence of maltose, one-third
appears as maltose, whilst the remainder appears as the stable
dextrin, an apparent resting stage having been reached exactly as
described by Brown and Morris (*loc. cit.*). The question arises,
however—Is the stable dextrin formed when amylopectin or
$\alpha\beta$-hexa-amylose is hydrolysed in absence of maltose ? This ques-
tion was answered by studying the hydrolysis of $\alpha\beta$-hexa-amylose
and of the stable dextrin in absence of maltose.

If the velocities of hydrolysis were identical in both cases, the
answer would be in the affirmative. We find, however, that
$\alpha\beta$-hexa-amylose is hydrolysed nearly three times as rapidly in
absence of maltose as it is in presence of maltose or when the stable
dextrin itself is hydrolysed under identical conditions. Since we
have satisfied ourselves that this difference cannot be attributed
to any conceivable disturbing factor, we can only conclude that
the stable dextrin is not produced when $\alpha\beta$-hexa-amylose is hydro-
lysed with malt diastase under the conditions described in absence
of maltose.

When starch paste is treated with malt diastase, two distinct
phenomena occur, *viz.*, saccharification and " liquefaction." The

optimum temperature of the former is 55°, and that of the latter about 70°. The term "liquefaction" is an expression of the fact that when starch paste is treated with malt diastase it loses its viscosity and is transformed into a limpid solution of so-called soluble starch,* a change we now know to be due to the dephosphating of the amylopectin. Since, therefore, the two phenomena, saccharification and liquefaction, are quite distinct, there was no reason to suppose that their temperature optima were the same. Our results show that the optimum temperature of hydrolysis of αβ-hexa-amylose by malt diastase, like that of α-hexa-amylose, is near 50°.

It has long been known that when a solution of malt diastase or an extract of malt is heated above 65°, a distinct change is brought about in the enzyme, restricting its chemical activity. No satisfactory explanation of this phenomenon has heretofore been adduced. The mechanism of the transformation of αβ-hexa-amylose at 50° and 70° respectively is explained by the following skeletal formulæ for this amylose, in which the dotted lines show the direction in which the fission takes place.

At 50°.   At 70°
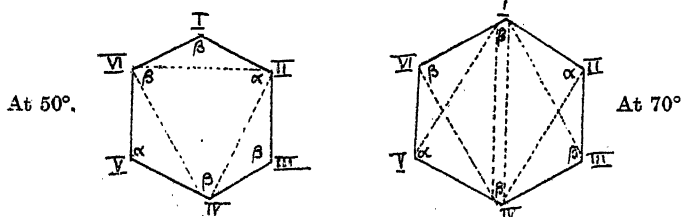
We find that at 50° malt diastase causes a fission between the linkings at II, IV, and VI, giving rise to three dihexose molecules as above mentioned. At 70°, on the other hand, the enzyme acquires the property of breaking the chain at linkings I and IV, giving rise to two trihexose molecules which are capable of undergoing further fission at linkings I—III, I—V, II—IV, and IV—VI, giving rise to two dihexose molecules and two hexose molecules.

The production of glucose by the hydrolysis of starch with malt diastase at 70°, first pointed out by Ling and Baker (J., 1895, **67**, 702, 739) and confirmed by Ling and Davis (*J. Fed. Inst. Brewing*, 1902, **8**, 475; J., 1904, **85**, 16), has been misunderstood by many chemists as being due to the action of the enzyme maltase, which we may point out, is no longer active above 55°. The total quantity

* Soluble starch prepared in this way shows slight cupric-reducing power even if prepared at so high a temperature as 75°, for at that temperature malt diastase still shows some very slight saccharifying power towards amylose. Both saccharifying and liquefying power are destroyed at 80°

of glucose produced under these conditions is 10—11% of the starch.   It is shown to be derived exclusively from the hydrolysis of β-glucosidomaltose.

The existence of the stable dextrin was first recognised by Brown and Morris in 1885 (*loc. cit.*) as an invariable product of the hydrolysis of starch paste by malt diastase at 50°, and the determination of its nature and constitution is a problem of the highest importance alike from the academic and practical points of view. To the chemist, the existence of the stable dextrin has presented a barrier which seemed unsurmountable in arriving at any definite conclusions regarding the constitution of starch, whilst to the industrialist it has a special economic importance.

Although it has not been found possible to arrive at definite conclusions regarding the constitution of the stable dextrin from the work of earlier investigators when viewed from the present state of our knowledge, most of it has proved invaluable to us. Indeed, progress would have been impossible without the technique laid down by such workers as Horace T. Brown in a field of chemistry such as that of the polysaccharides, which abounds with pitfalls.

The course we adopted in attacking the problem of the constitution of the stable dextrin was to study first the origin of the dextrin, secondly the conditions under which it is formed, and lastly the nature of its products of hydrolysis with malt diastase. After having worked in these directions, we have arrived at definite conclusions regarding the nature of the compound from a study of its products of hydrolysis with malt diastase under various conditions.

In their work on the stable dextrin, Brown and Millar (J., 1899, 76, 315) appear not to have paid sufficient attention to its isolation in quantitative yield and in a state in which as little alteration as possible had taken place, a matter of fundamental importance if any conclusions regarding the nature and constitution of the substance are to be drawn from experimental work with it.   Our first efforts, therefore, were to discover a method by which the dextrin could be isolated quantitatively in the same condition as it is present in a starch conversion carried down to the apparent resting stage.   We had therefore constantly to keep in mind the point that at no stage in its isolation and purification must any change be brought about in the dextrin molecule.   Brown and Millar (*loc. cit.*) employed an elaborate method of purifying their product, and, from considerations which we will now put forward, we believe the treatment to which they subjected it must have given rise to modifications in its character.

We have already stated that in the production of the stable

dextrin one-third of the $\alpha\beta$-hexa-amylose (11·1% on the starch) is hydrolysed with the production of maltose, which together with the 66·6% of α-hexa-amylose (converted entirely into maltose) gives a total of 77·7% of the starch converted into maltose in a conversion brought to the stable dextrin stage, the remaining 22·3% appearing as stable dextrin. We have found that when potato starch is hydrolysed at about 40° with precipitated malt diastase from ordinary brewery malt having a diastatic power on the Lintner scale of about 30°, until the percentage of apparent amylose (estimated as maltose), expressed on the original dry starch, reaches 80·8°, the specific rotatory power is invariably $[\alpha]_D$ 147—148°. When such a conversion liquid is fermented with yeast, 77·5—78·0% of the original reducing power disappears and the residue shows $[\alpha]_D$ 185° and R 14. The yield of this unfermentable residue calculated on the anhydrous starch is uniformly 22%. Here, then, we have effected a quantitative fractionation of a starch conversion brought to the stable dextrin stage into two portions in the proportion of 78% of the former and 22% of the latter, which we regard as the stable dextrin. We shall now show that the rotatory and the reducing power of these fractions account exactly for the constants of the mixture within the limits of experimental error. Thus $[\alpha]_D$ —1/100 $(78 \times 138 + 22 \times 185) = X = 148·3$, where X is the specific rotatory power of the resulting mixture. Again, $R - 1/100$ $(78 \times 100 + 22 \times 14) = Y = 81·0$, where Y is the reducing power of the mixture.

If, now, we examine the constants recorded by Brown and Millar, expressed on the same basis, we shall find that they do not account for the optical and reducing values of the stable dextrin mixture as determined by us. Thus :

$$[\alpha]_D \ 1/100 \ (77·8 \times 138 + 22·2 \times 195·5) = X = 150·7°,$$
and $\quad R \ 1/100 \ (77·8 \times 100 + 22·2 \times 6) = Y = 79·1.$

From these values it will be seen that the calculated value of the specific rotatory power of the mixed products is higher, whilst that of the reducing power is lower, than the same constants calculated from our values.

It will be shown that when the stable dextrin is hydrolysed in presence and in absence of maltose, there is no appreciable difference in the velocity of the reaction, which only becomes perceptible in the later stages after the reaction has proceeded for a protracted period.

The velocity of hydrolysis of the stable dextrin increases in the range 30—40° with a maximum at 40° and then decreases. In the initial stages the optimum temperature varies according to the period of hydrolysis.

When a solution of the stable dextrin is hydrolysed for a pro-
tracted period at 30—40°, the conversion liquid has the constants
$[\alpha]_D 140 \cdot 5°$ and R 112·0, indicating distinctly the presence of glucose.
When such a conversion is subjected to fermentation with yeast,
90% of the total solids are fermented away.   If, now, the conversion
liquid is treated with phenylhydrazine acetate, it gives only a small
quantity of insoluble glucosazone but a large amount of pure malt-
osazone.   Brown and Millar (loc. cit.) found that when stable dextrin
was hydrolysed with malt extract it gave equal parts of maltose
and glucose.   We have not been able to confirm this statement
with precipitated malt diastase, and therefore the production of
the large amount of glucose from the stable dextrin must be attri-
buted to the presence of maltase in the malt extract employed by
Brown and Millar, which they believed was free from this enzyme
(compare Ling and Nanji, Biochem. J., 1923, 17, 593).   When the
stable dextrin is hydrolysed with malt diastase in presence of 80%
of maltose, it gives rise to a mixture of equal parts of maltose and
isomaltose, whilst with maltase it yields isomaltose, and with
emulsin, maltose and glucose.

There is little doubt that the basal unit of the stable dextrin is
composed of four hexose residues.   This will be clear from the
fact that the dextrin is produced from $\alpha\beta$-hexa-amylose together
with a third of its weight of maltose, which must necessarily entail
the production of a substance containing four hexose residues.   The
questions now arise—What becomes of the residual valencies on
the rupture of the $\alpha\beta$-hexa-amylose structure, and is the stable
dextrin thus produced an open-chain compound or a closed-chain
compound ?   The molecular weight of the stable dextrin is of the
order of 1923, from which it may be conceived that it is an open-
chain compound containing twelve hexose residues.   This would
account for both its reducing power and the molecular weight, but
we have scarcely any practical grounds on which we can justify
this view.   On the other hand, it cannot be a completely closed
chain structure, because it possesses a reducing power R 14.   After
having carefully considered both these possibilities and accounted
for all the known properties of the stable dextrin, we have drawn
the conclusion that it is partly composed of a closed-chain and
partly of an open-chain complex, the basal molecule of both of
which is the same.   It is thus in fact not a single substance but a
mixture, possibly a co-ordinated mixture of these two components.
The next thing we have to decide is the constitution of the open-
chain constituent, which primarily involves the determination of
the reducing group.   Is it the maltose end of the C_{24}-unit that
contains the carbonyl group, or the isomaltose end ?   It will be

seen that in all the three possible structures put forward for the constitution of $\alpha\beta$-hexa-amylose (p. 644) the C_{24} residues on I and II have the maltose residue in the reducing end of the chain, whilst in III the reducing group is in the *iso*maltose residue as follows :
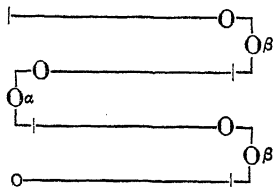
When we study the reducing power, R, of the different derivatives of starch, especially those of high molecular weight, we find that the value of R diminishes almost proportionately as the molecular weight increases, whilst the specific rotatory power increases directly with the molecular weight. We are thus brought to recognise a relation between the rotatory and the reducing powers of the products of hydrolysis of starch first assumed by C. O'Sullivan in his papers published between 1876 and 1882, and later strongly insisted on by H. T. Brown and his co-workers. The difference, however, between the way in which we adopt this rule and that in which it was put forward by the earlier workers lies in the fact that the latter interpreted their results in terms of maltose only as a standard reducing substance and a non-reducing dextrin, whereas we have proved the existence of substances, *e.g.*, β-glucosidomaltose and *iso*maltose, the constants of which differ from those of maltose. It should be added that Brown and Millar in their paper recognised that their so-called stable dextrin was a reducing substance. To give an example of the application of this rule, β-glucosidomaltose has R 66 compared with that of maltose, R 100. Thus, the above structure, having the *iso*maltose residue as the reducing terminal group, might be expected to have R 40—42, if we take R 80—84 as the standard for *iso*maltose. When the stable dextrin isolated by us is submitted to repeated fractionation with 86% alcohol, a fraction soluble in alcohol is obtained having the constants $[\alpha]_D$ 174·6° and R 38·7. A 4·1% solution of this fraction gave a mean depression 0·110°; $M = 693$.

This molecular weight is identical with that of the maltodextrin-β of Ling and Baker (*loc. cit.*), $C_{24}H_{42}O_{21}$, having the constants $[\alpha]_D$ 173·5° and R 43, which are substantially the same as those of the substance extracted by alcohol. We are, in fact, led to the conclusion that the stable dextrin as isolated by us is a mixture of two components, one of which is an open-chain compound identical with the maltodextrin-β of Ling and Baker, and the other a closed-

chain substance of a very much higher molecular weight and having the same C_{24}-unit representing its closed-chain basal structure.

The relative proportions of these two components can be readily arrived at from the reducing power of the stable dextrin mixture, R 14, and that of its reducing component which has R 43. This would distinctly point to the fact that the two components are present in the proportion of one part of maltodextrin-β to two parts of the tetra-amylose corresponding to this maltodextrin. With regard to the fate of the residual valencies on fission of the αβ-hexa-amylose structure, the low reducing power of our stable dextrin can be accounted for only by the fact that the residual valencies are linked up partly on fission of the αβ-hexa-amylose, giving rise to a tetra-amylose corresponding to maltodextrin-β. In arriving at the constitution of this tetra-amylose, we have to deal with three possibilities corresponding to the three structures previously proposed for the basal unit of αβ-hexa-amylose. These are represented as follows :

α β - Hexa-amylose.

(1)   (2)   (3)

maltodextrin-β.   maltodextrin-β.

Tetra-amylose corresponding to maltodextrin-β.

I - Carbinol group.
o - Carbonyl group.
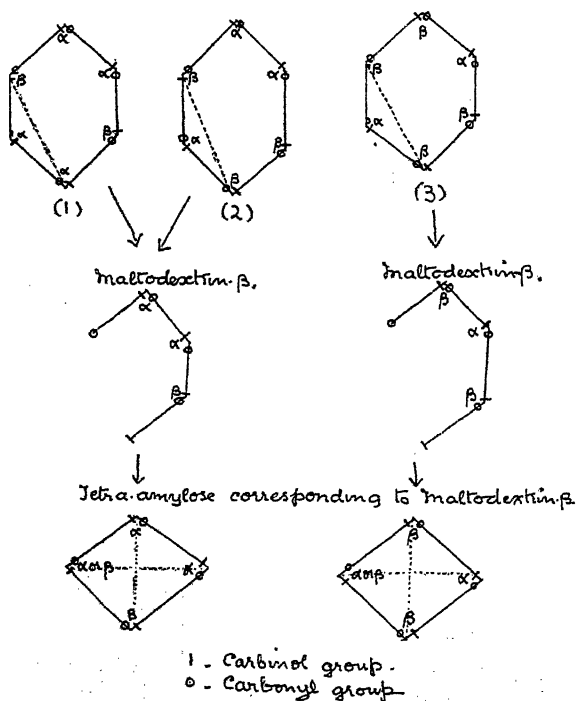
The maltodextrin derived from (1) and (2) is, it will be seen, one and the same substance, which differs from that derived from

(3) in that it has a maltose group in the carbonyl end of the molecule whilst the latter has an *iso*maltose grouping in the carbonyl end. Further, a maltodextrin of the type derived from either (1) or (2) should have at least R 50 compared with that of maltose, R 100, whilst the maltodextrin isolated by us possessed only R 38·8. The maltodextrin derived from (1) or (2) is also incapable of giving rise to maltose and glucose, as we have observed on hydrolysis with emulsin. With maltase it would give rise to considerable amounts of glucose, which also has not been observed. The malto-dextrin derived from (3), on the other hand, would be expected to have R 40—42 compared with that of *iso*maltose, R 80—84. With maltase it would give *iso*maltose and with emulsin it would be hydrolysed to a mixture of maltose and glucose. All these require-ments are in agreement with the conclusions already set forth for our maltodextrin, which can therefore only be derived from αβ-hexa-amylose having the structure (3).

Maltodextrin-β, $C_{24}H_{42}O_{21}$, described by Ling and Baker (*loc. cit.*), having $[\alpha]_D$ 173·5° and R 43, would therefore have the following constitution :
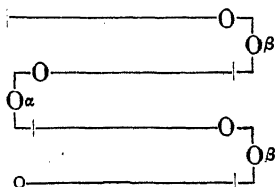
Our stable dextrin, therefore, may be represented by the following skeletal formula composed of 2 mols. of polymerised tetra-amylose corresponding to maltodextrin and 1 mol. of maltodextrin :
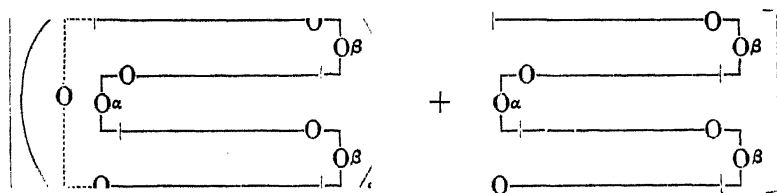
Maltodextrin-α described by Ling and Baker, $C_{36}H_{62}O_{31}$, has the constants $[\alpha]_D$ 180° and R 33·0. It will be seen that the value of R here again is nearly one-third of that of maltose, which further substantiates its molecular weight and also its formula. It is thus composed of six hexose residues, having a maltose residue in the carbonyl end of the compound. If there were an *iso*maltose unit in the carbonyl end of the chain, the value of R that would be required would be 27—28. It will be remembered that malto-

dextrin-α is formed when starch is hydrolysed with malt diastase at 70°. This renders the assigning of its constitution a comparatively easy task, because there is only one possibility for the fission of the αβ-hexa-amylose structure. We have seen that at this temperature fission takes place between two diametrically opposite linkings, with the formation of β-glucosidomaltose. Maltodextrin-α must therefore be regarded as an intermediate product in this degradation of αβ-hexa-amylose to β-glucosidomaltose, in the formation of which the fission of only one linking is concerned instead of the two as in the formation of β-glucosidomaltose. This, therefore, shows that in the formation of maltodextrin-α the αβ-hexa-amylose ring is simply opened up with the formation of a straight-chain compound containing six hexose residues. The constitution of maltodextrin-α and its relation to αβ-hexa-amylose and to β-glucosidomaltose will be clear from the following representation:

αβ-Hexa-amylose.   Maltodextrin-α.   β-Glucosidomaltose.
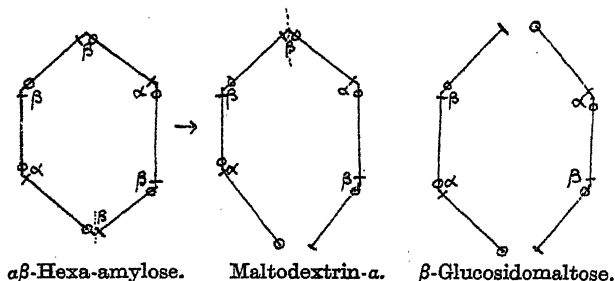
E X P E R I M E N T A L.

Hydrolysis of αβ-Hexa-amylose in Presence and Absence of Maltose. —For the purpose of these experiments two solutions were prepared. One contained 1·72 g. of αβ-hexa-amylose in 100 c.c. and the other 4·5 g. of a mixture of two parts of maltose and one part of αβ-hexa-amylose in 100 c.c. Of these solutions, 10 c.c. portions were measured into a series of test-tubes, which were placed in a metal stand and immersed in a water-bath at 55° so that the level of the water was just above the surface of the solution. A solution of precipitated malt diastase containing 1 mg. of the enzyme per c.c. was raised to 55°, and 2 c.c. of it were added to each of the test-tubes containing 10 c.c. of the solutions at the same temperature. One tube from each of the two series was withdrawn at different intervals, and the contents were washed into a 100 c.c. flask containing a drop of 10% caustic soda solution. The solutions were then made up to 100 c.c. and titrated against Fehling's solution. A 100 c.c. portion of the 4·5% solution containing a mixture of

2 parts of maltose and 1 part of αβ-hexa-amylose was converted side by side of the test-tube experiments with 20 c.c. of diastase solution at 55° for the purpose of determining the final constants.

The results are shown in the following table :

Rate of Hydrolysis of αβ-Hexa-amylose in Presence and in Absence of Maltose.

Time in hours.	Percentage of apparent maltose produced.		Percentage of apparent maltose produced from hexa-amylose.	
	Hexa-amylose and maltose.	Hexa-amylose alone.	In presence of maltose.	In absence of maltose.
½	70·60	63·3	17·42	63·3
1	75·04	66·8	29·78	66·8
2	—	70·6	—	70·6
3	77·97	73·0	38·12	73·0
4	79·35	73·2	42·0	73·2
5	79·70	73·0	42·98	73·0
6	79·70	73·4	42·98	73·4

The specific rotatory power of the solids in the solution containing αβ-hexa-amylose and maltose after being incubated at 55° for 6 hours was $[\alpha]_D$ 146·5—147°, whilst, when the incubation period was prolonged for a week, it was $[\alpha]_D$ 138·2°, the reducing power being R 98·1. When the last-mentioned conversion liquid was inoculated with *Sac. cerevisiæ*, 89% of the reducing power, expressed as maltose, had disappeared after fermentation was complete, thus indicating the presence in the fermented liquid of some 11% of *iso*maltose (expressed on the original solids in the mixture), which sugar was identified by its phenylosazone.

When a solution of αβ-hexa-amylose alone was incubated at 55° for a week with malt diastase, the constants of the dissolved solids were $[\alpha]_D$ 141·0° and R 91·0. After fermentation, about one-third of the total solids in the solution had disappeared and the remaining portion had a reducing power of R 79·4. The dissolved solids were shown to consist of *iso*maltose, which was identified by the osazone.

Velocity of Hydrolysis of the Stable Dextrin and of αβ-Hexa-amylose by Malt Diastase at 55°.—To determine the velocity of hydrolysis of the stable dextrin and of αβ-hexa-amylose with malt diastase, a solution containing 1·13 g. of the stable dextrin (which was prepared in the manner to be described later) and another containing 1·7 g. of αβ-hexa-amylose were submitted to the action of malt diastase at 55° in the manner described in the previous section for αβ-hexa-amylose, the quantity of diastase used being 0·02 g. per 100 c.c. The following table gives the results :

Time in hours.	Percentage of stable dextrin hydrolysed in terms of maltose. A.	Percentage of αβ-hexa-amylose hydrolysed in terms of maltose. B.	Calculated percentage of potential stable dextrin produced from αβ-hexa-amylose hydrolysed in terms of maltose.* C.
½	—	63·3	45·0
1	—	66·8	50·2
2	—	70·6	55·9
3	21·0	73·0	59·5
4	—	73·2	59·8
5	—	73·0	59·5
6	26·2	73·4	60·1
16	40·0		
64	59·8		

* The values in column C were calculated from those in column B by the formula 100 $(B - 33\cdot3)/66\cdot6$, in which B represents the values given in the column under that letter. It has been shown that αβ-hexa-amylose yields one-third of its weight of maltose when hydrolysed in presence of maltose. The difference, $B - 33\cdot3$, would therefore represent the percentage of maltose derived from the remaining 66·6% of stable dextrin.

Determination of the Optimum Temperature of Hydrolysis of αβ-Hexa-amylose with Malt Diastase.—Portions of 25 c.c. of a solution containing 1·2 g. of αβ-hexa-amylose in 100 c.c. were measured out into each of a series of flasks and incubated at the undermentioned temperature in presence of 2·5 c.c. of a solution containing 1·25 mg. of precipitated malt diastase. At the end of 1½ hours the solutions were rapidly raised to the boiling point, cooled, and made up to 100 c.c. The reducing power, expressed in terms of maltose, was then determined iodometrically in 50 c.c. of the liquid by the method of Baker and Hulton (*Biochem. J.*, 1920, **14**, 754). The results are given in the following table :

Temp.	30°	40°	50°	60°	70°
Rel. quant. of maltose produced ...	2·7	3·0	3·4	2·9	1·8

Velocity of Hydrolysis of αβ-Hexa-amylose at 70°.—A solution (250 c.c.) containing 1·2 g. of αβ-hexa-amylose was treated with a solution of precipitated malt diastase which had been previously treated at 70° for ½ hour, and the velocity of hydrolysis was followed as usual by determining the reducing power at definite intervals. The results are shown in the table, where a is the percentage of αβ-hexa-amylose hydrolysed to β-glucosidomaltose :

Time (min.)	15	30	150	210
a.	6·7	9·3	29·7	39·9

Preparation of the Stable Dextrin.—A paste containing 7—8% of prime potato starch per 100 c.c., representing about 1 kg. of starch (containing 20% of moisture), was treated with 0·5 g. of precipitated malt diastase at 40°. We have purposely avoided the use of malt extract, which not only introduces impurities difficult to remove from the final dextrin, but also contains the enzyme

maltase, which would modify the constants of the conversion. Further, we did not consider it safe to hasten the liquefaction of the paste by raising it to the optimum temperature of liquefaction in presence of a small quantity of diastase before adding the main quantity at 40°, since this unquestionably alters to some extent the course of the conversion. The hydrolysis was allowed to continue at 40° until the constants approached $[\alpha]_D$ 148° and R 80·8.

It was found preferable to stop the conversion when it stood at R 80, since during the time required for raising the liquid to the boiling point a slight increase in the reducing power takes place and usually it is found to be R 81 after boiling. The filtered conversion liquid was concentrated to a thin syrup, which was poured while hot in a thin stream into a large volume of 95% alcohol so that the final strength of the alcohol in the mixture was about 85—86%. The precipitated dextrin was then kneaded for several hours with alcohol of the strength just mentioned. The crude dextrin removed from the alcoholic liquid amounted to 450 g. for every kilogram of anhydrous starch employed; it had a reducing power corresponding with 60% of maltose. It was dissolved in sufficient water to make a 15% solution, and, after boiling off the alcohol, it was sterilised and fermented with fresh brewers' yeast for about a week, when fermentation was complete. It may be remarked that fermentation of maltose proceeds slowly in presence of the colloidal dextrin. Attempts to separate the stable dextrin and maltose by dialysis proved unsuccessful, even when the dialysis was carried out against a strong current of running water.

If the fermented product had a reducing power above R 14, it was again fermented until this point was reached, when the solution no longer gave a crystalline phenylosazone. After decolorising with norit, the solution was dialysed to free it from mineral matters. It was then concentrated on a water-bath to a syrup, which was spread on a level glass surface placed in contact with a metallic plate at 40°. In this way a perfectly dry film was obtained in about 12 hours. The film was removed with a knife and powdered. It was thus obtained as a slightly hygroscopic, white powder having the constants $[\alpha]_D$ 185° and R 14. The fact already mentioned that these constants are in harmony with those of the stable dextrin-maltose mixture shows that no alteration has been brought about by the method of isolating the dextrin. The yield is almost theoretical, i.e., about 22% of the dry starch employed.

The product thus obtained was quite free from ash and nitrogen, and on submitting its aqueous solution to dialysis for a long period no change in its constants was observed. With alcohol, however, it behaved peculiarly in that on fractionation its specific rotatory power increased whilst its reducing power decreased. A 9·1%

Variations in the optimum temperature for the hydrolysis of the stable dextrin with different periods of hydrolysis.

Relative amounts of apparent maltose produced.
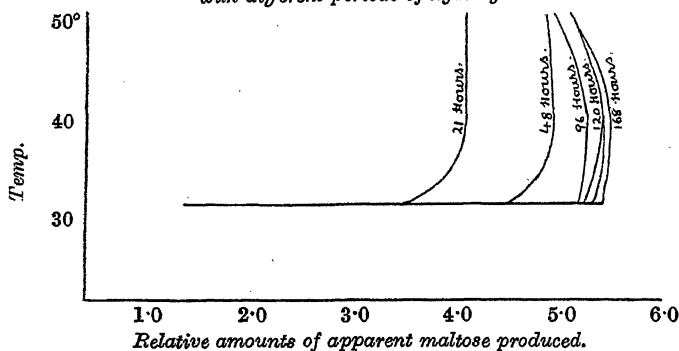
Rate of hydrolysis of the stable dextrin in presence and in absence of maltose.

Per cent. of stable dextrin hydrolysed expressed as apparent maltose.

····· *In presence of maltose.*
——— *In absence of maltose.*
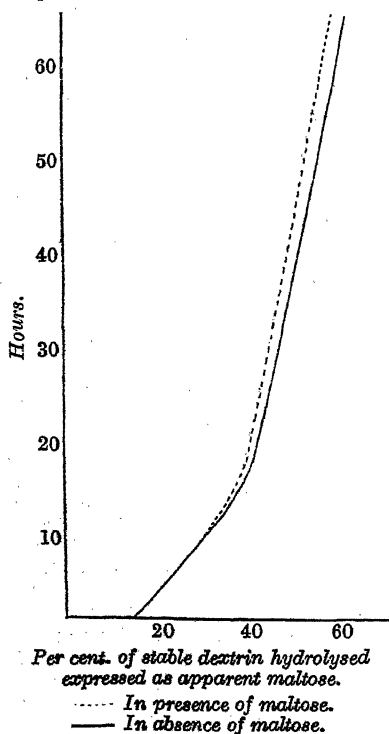
solution of the preparation gave a mean depression of 0·088°; M 1923, which is very much lower than that of Brown and Millar, *viz.*, M 6221. It must be mentioned, however, that the molecular weight of our product also increases on fractionation but not on dialysis. Our stable dextrin is acted upon slowly by maltase, giving *iso*maltose, and by emulsin, giving maltose and dextrose. Having now dealt with the properties of our stable dextrin, we shall pass on to a description of the different quantitative experiments on its transformation with diastase under different conditions.

Velocity of Hydrolysis of the Stable Dextrin in Absence of Maltose and in Presence of 78% *of Maltose.*—A 2·2% solution of the stable dextrin and a 10% solution of a starch conversion containing 22% of the stable dextrin and 78% of maltose were treated at 55° with 0·02 g. of precipitated malt diastase for every 100 c.c. of the solution, and the velocity of hydrolysis was followed in the usual manner by determining the reducing power at different intervals. The results are shown graphically in the above curves.

Velocity of Hydrolysis of the Stable Dextrin at Different Temperatures.—A 2·2% solution of the stable dextrin was treated with 0·15 g. of precipitated malt diastase for every 100 c.c. of the solution, together with a little toluene, at the different temperatures indicated in the following table, and the velocity was followed in the usual manner by determining the relative amounts of maltose produced.

Time in hours.	Relative amount of maltose produced at $T°$.		
	30°.	40°.	50°.
0	2·1	2·1	2·1
21	6·8	8·0	8·0
48	8·8	9·8	9·6
96	10·4	10·6	9·8
120	10·6	11·0	10·2
144	10·8	11·0	10·2
168	11·0	11·2	10·2

The hydrolysis of starch by barley and malt diastase is epitomised in the following scheme.
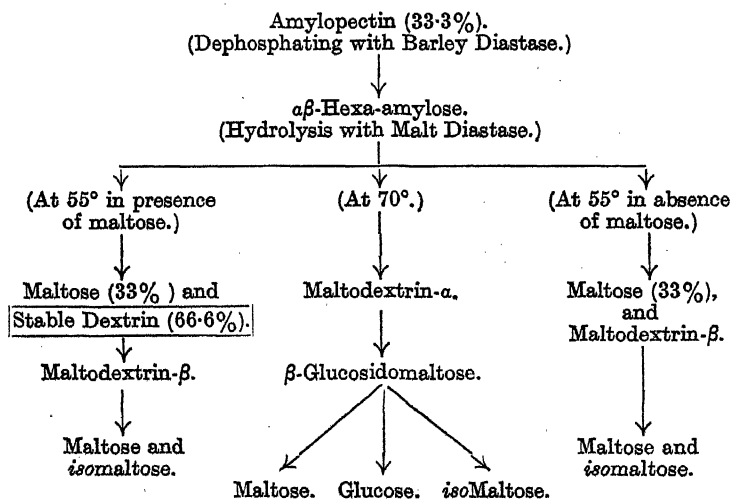
Amylopectin (33·3%).
(Dephosphating with Barley Diastase.)

↓

$αβ$-Hexa-amylose.
(Hydrolysis with Malt Diastase.)

(At 55° in presence of maltose.)   (At 70°.)   (At 55° in absence of maltose.)

↓

Maltose (33%) and Stable Dextrin (66·6%).   Maltodextrin-$α$.   Maltose (33%), and Maltodextrin-$β$.

↓

Maltodextrin-$β$. $β$-Glucosidomaltose.

↓

Maltose and *iso*maltose.   Maltose.   Glucose.   *iso*Maltose.   Maltose and *iso*maltose.

BRITISH SCHOOL OF MALTING AND BREWING AND
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XCIV.—Studies on Starch. Part IV. The Nature of the Amylo-hemicellulose Constituent of certain Starches.

By ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI.

IN Part I of these studies (J., 1923, **123**, 2671) we have confirmed the observations of Schryver and his co-workers that certain starches, notably those of barley, wheat, rice, etc., contain a substance of the nature of a hemicellulose (see Schryver and Thomas, and Clayson and Schryver, *Biochem. J.*, 1923, **17**, 493, 497).

This " amylo-hemicellulose," as we prefer to designate it, is widely distributed in nature and occurs in considerable quantities, especially associated with starch, in the different starch-bearing fruits and seeds. It also appears to be present in leaves and stems and seems to be one of the principal constituents of the cell walls of such plants, formed at a very early stage of their development. In the different woods we have examined, it is also present in varying quantities. Since the main portion of the hemicellulose gives a blue iodine reaction, it might be confused in some cases, notably when present in woods, with starch. Another polysaccharide, which does not give an iodine reaction, present in starch to the extent of less than 1% was contained in the product isolated by us.

Our view, that the silica in the hemicellulose exists in organic combination with the polysaccharide as an ester, has now been confirmed, and we find that the whole of the silica is present in organic combination, the hemicellulose being a calcium-magnesium or iron salt of a silicic ester. The recent work of Pringsheim and Kusenack (*Z. physiol. Chem.*, 1924, **137**, 265) on lichenin is but another instance of the occurrence of such silicic esters. Indeed, our view is fast gaining ground that silica fulfils a very important *rôle* in plant metabolism, and the results of an extended investigation in this direction, mainly from an agricultural point of view, have already been published elsewhere (Nanji and Shaw, *J. Soc. Chem. Ind.*, 1925, **44**, 1T).

This hemicellulose is not acted on by the diastase of ungerminated barley even after prolonged incubation at 50°, whilst the other two constituents of the starches are hydrolysed or rendered soluble by this enzyme. We have thus a ready means of isolating the hemicellulose. It is hydrolysed by diastase of germinated barley (malt) and we have now ascertained the products of hydrolysis at different temperatures and the velocity of the reaction when this enzyme is employed.

Preliminary experiments showed that whilst there is no essential difference between precipitated malt diastase and a freshly-prepared

extract of malt, the latter is very much quicker in its action and brings about the hydrolysis more completely than precipitated malt diastase, which is uncertain in its action in the final stages, and leaves 15— 16% of the hemicellulose unhydrolysed. When a concentrated paste of the hemicellulose is hydrolysed with malt extract, and the liquid tested from time to time with iodine, it is found that the iodine coloration disappears rapidly and is not given either by the residuum or by the clear conversion liquid, but if the former be boiled with a little water, it again gives a strong blue colour with iodine.

Experimental.

Preparation of the Amylo-hemicellulose.—A 10% paste of wheat or rice starch (1 kilo.) is hydrolysed at 50° with a cold water extract of barley corresponding to about 200 g. of finely-ground barley. The mixture is kept at 50° for 12—24 hours, when the hemicellulose usually flocculates. The liquid is centrifuged and the flocculum of the hemicellulose is repeatedly washed on the centrifuge until the washings are free from reducing sugars. The flocculum is boiled with water and again submitted to the action of barley diastase and washed free of reducing sugars. Another method we adopted for freeing the hemicellulose from reducing sugars, which involved less trouble, consisted in transferring the flocculum to muslin bags, which were immersed in a current of running water. The process of osmosis was carried out in presence of a piece of camphor and was considerably expedited by alternatively raising and lowering the bags in the water. The flocculum, after being thus freed from the reducing sugars, was dehydrated with 90% alcohol and then with absolute alcohol, when it was obtained as an amorphous, white powder practically insoluble in cold water. The yield of the product was about 7—8% from wheat starch and 15% from rice, which are below the amount actually found by analysis, as will be shown later. The loss incurred, principally during washing, is only of the order of about 3%. The product is quite free from pentose, and on hydrolysis with mineral acids silica separates out from the hydrolysed liquid; and this is the reason why pastes of starches, such as barley, wheat, rice, etc., which contain this hemicellulose, always remain turbid, even on complete hydrolysis. In hot water it gives a gelatinous paste which with higher concentration almost sets to a gel on cooling. The hemicellulose thus obtained is quite free from nitrogen, although it is never free from ash. The ash of several preparations was uniformly 1·2—1·3%, which consisted principally of silica, phosphoric acid, calcium, magnesium, and iron. The amounts of calcium, magnesium, and phosphoric acid varied considerably, although the

percentage of silica, which constituted the major portion of the ash, was remarkably constant between 0·83—0·92% (SiO_2).

Hydrolysis of Amylo-hemicellulose with Malt Diastase.—When a paste of the hemicellulose is submitted to the action of malt diastase, it is hydrolysed rapidly, giving exclusively maltose as the final product of its hydrolysis, the velocity of the reaction being dependent on certain factors. Thus a part of the hemicellulose always remains in solid suspension in the colloidal solution of the remainder, and the latter portion is rapidly hydrolysed, whilst the portion in suspension is unaffected. This introduces difficulties in the studies on the kinetics of its hydrolysis with malt diastase under different conditions. It would have been possible to overcome this difficulty and get a homogeneous substrate by heating it in an autoclave which had a liquefying action, but as we intended to get a true picture of the behaviour of the hemicellulose, exactly as it exists in nature, with diastase, we surmounted this difficulty by employing a dilute solution and so arranging the amounts of enzyme and the substrate (in colloidal solution) that the latter was not completely hydrolysed.

Optimum Temperature for the Hydrolysis of the Hemicellulose with Malt Extract.—Several 0·25 g. portions of the hemicellulose were each transferred carefully to 100 c.c. flasks and thoroughly gelatinised with 50 c.c. of water, and after bringing their contents to the temperatures indicated below, they were treated with 2·5 c.c. of a cold water extract (1 part of malt to 2·5 parts of water) of low-dried malt, the latter being brought to the respective temperatures before addition to the hemicellulose solution. A blank solution containing the equivalent quantity of malt extract in 50 c.c. of the solution was also kept side by side with each experiment. The hydrolysis was stopped at the end of 1 hour by rapidly bringing the solutions to the boiling point. The solutions, after cooling, were made up to 100 c.c. and filtered, and the reducing power of 50 c.c. of the filtrate was determined iodometrically. The relative amounts of maltose produced after correcting for the reducing power of the malt extract used are as follows, from which it will be seen that the optimum is about 50—55°, whilst there is practically no hydrolysis of the hemicellulose taking place at 70°.

Temperature	30°	40°	50°	55°	60°	70°
Rel. amounts of maltose produced	6·0	6·5	7·0	7·0	6·0	0·0

Rate of Hydrolysis of Hemicellulose at Different Temperatures.— A 1·6% paste of the hemicellulose was treated at the different temperatures with 5·0 c.c. of a cold water extract of malt (prepared as before) for every 100 c.c. of the paste. 50 c.c.-Portions were withdrawn at different intervals and the action was stopped by

boiling. The portions were cooled, made up to 100 c.c., filtered, and the rate of hydrolysis followed as usual by determining the reducing power after correcting for that of the malt extract used. The results are given in the following table, where t is the time in minutes and m the relative amounts of maltose produced :—

Velocity of Hydrolysis of the Hemicellulose at Different Temperatures.

30°.		50°.		70°.	
t.	m.	t.	m.	t.	m.
15	10·4	15	18·5	15	3·5
30	15·6	45	19·5	30	3·6
105	19·7	60	20·0	45	3·7
165	20·6	120	20·0	60	3·9
285	23·2	300	20·8	120	4·2
345	23·3	360	22·6	300	5·0
		450	23·1		

When a paste of hemicellulose was treated for a protracted period with a solution of precipitated malt diastase at 50°, and the liquid filtered from the insoluble residuum, the solids in the filtrate approximated to about 84—85% of the original hemicellulose taken, and had the constants $[\alpha]_D - 137\cdot4°$ and R 98·3. If a little of the conversion liquid was treated with *Saccharomyces cerevisiæ*, the sugar was completely fermented away, as observed by the complete disappearance of reducing power. With phenylhydrazine acetate it gave maltosazone, m. p. 193°, which, when examined microscopically, was quite free from crystals of the *iso*maltosazone type. The residue from the above conversion gave a bluish-purple coloration with iodine. It was boiled again with water and, on reconverting with precipitated malt diastase, gave exclusively maltose. This was further confirmed by hydrolysing hemicellulose with a freshly prepared malt extract (which hydrolyses hemicellulose more rapidly) and examining the fermentability of the sugar in the conversion liquid, which was also completely fermented away. There is no doubt, therefore, that the sugar produced by the complete hydrolysis of hemicellulose is exclusively maltose. This fact distinctly shows that it is a derivative of α-hexa-amylose, and this would be further substantiated by the characteristic similarity in the behaviour of both α-hexa-amylose and the hemicellulose with malt diastase at 70°. The differences in the physical properties of these two substances would be, in all probability, due to the esterification of the α-hexa-amylose with silicic acid, and we hope to gain further information on this point by attempting to prepare synthetically the silicic esters of the carbohydrates.

The relationship between hemicellulose and polymerised α-hexa-

amylose and their hydrolysis with diastase are epitomised in the following scheme.

```
┌──────────────────── Hemicellulose
│  ┌  ┌                        ↑
│  │  │                        ┆
│  ┤  │        (Phosphating and Silicifying)
│  ┤  ┤            Amylose (66·6%)
│  ┤  ┤            Crystalloidal (25·0%)
│  ┤  ┤            Colloidal (75·0%)
│  ┤  ┤        (With Barley or Malt Diastase)
│  │  │                        │
│  └  └                        ↓
└────────────────────→ Maltose
```
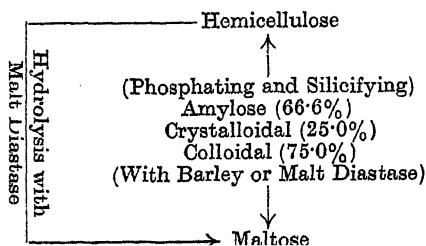
Determination of Amylo-hemicellulose in Starches.—The hemicellulose content of starches has been found to vary within wide limits and to depend to a very large extent on the state of division of the amylaceous material and the degree of fractionation to which it has been submitted during manufacture. It can be readily estimated as follows : A known weight of the starch is gelatinised thoroughly by boiling and treated at 50° with barley diastase corresponding to about 10 g. of barley for 2·5 g. of the dry starch. The conversion liquid is made up to 200 c.c. together with the hemicellulose flocculum and filtered. The density of the filtrate is taken and from the excess density the percentage of the total solids is determined by dividing it by the factor 3·95. Two-thirds of the solid matter in the conversion liquid being maltose, and the rest αβ-hexa-amylose, the former is expressed as anhydrous starch by multiplying by the factor 0·9473. The weight of total solids, after correction for the water of hydration of maltose, is subtracted from the weight of the anhydrous starch taken, and the difference gives the hemicellulose. Rice starch contains 19·15%, wheat 10·0%, and barley 7·68%, but these values vary according to the process of manufacture adopted.

XCV.—*The Thermal Decomposition of Nitrogen Pentoxide.*

By HERBERT S. HIRST.

IN recent years considerable interest has centred round the subject of the velocity and mechanism of unimolecular reactions. For the simplest type, namely, homogeneous reaction in the gaseous phase, there have been many attempts to develop a theoretical interpretation, and various expressions for the rate have been published from time to time. Very convenient summaries of the work done on this subject have been presented by Tolman (*J. Amer. Chem. Soc.*, 1921, **43**, 269) and by Harned (*J. Franklin Inst.*, 1923, **196**, 181). Special reference may also be made to the recent important communications of Christiansen (*Z. physikal. Chem.*, 1922, **103**, 91) and of Christiansen and Kramers (*ibid.*, 1923, **104**, 451). All the equations obtained are of the same nature, that is to say, the reaction velocity in all cases follows an exponential law of the type $k = s\epsilon^{-Q/R\theta}$, where k is the velocity coefficient. It is in the interpretation of the quantities s and Q that the differences arise. The fundamental questions of the nature of the primary activation which precedes chemical reaction and of the mechanism of reaction itself are still largely problematical. The difficulty of any definite decision is considerably augmented in the case of a homogeneous unimolecular reaction, owing to the almost entire lack of experimental evidence whereby the many and varied theories may be put to the test. Until the present year, the experiments of Trautz and Bhandarkar (*Z. anorg. Chem.*, 1919, **106**, 95) on the dissociation of phosphine provided the only numerical data of the reaction velocity of what was thought to be a truly homogeneous non-catalytic, unimolecular reaction in the gaseous phase. Recently, however, it has been shown by Hinshelwood and Topley (*J.*, 1924, **125**, 393) that the reaction is by no means homogeneous, the wall effect being very pronounced, and that, consequently, no valid test can be applied by the use of these results. As regards the decomposition of nitrogen pentoxide, first investigated and shown to be unimolecular in nature by Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 53), this was supposedly ruled out, although quite homogeneous, by the discovery of an autocatalytic effect (Daniels, Wulf, and Karrer, *ibid.*, 1922, **44**, 2402). Up to the present, then, there seems to be absolutely no evidence that a true unimolecular reaction in the gaseous phase does ever occur, and in view of this Hinshelwood and Topley (*loc. cit.*) have pointed out that an investigation of the reason for such a non-existence may be

of greater importance than a continual accumulation of unverifiable theory.

It is one of the purposes of the present paper, however, to show that it is by no means improbable that the dissociation of nitrogen pentoxide may yet prove to be an example of a reaction which fulfils all the requirements of a true gaseous unimolecular decomposition. An investigation by the author of the chief evidence on which the assumed autocatalytic nature of the process depends has failed to substantiate this evidence and indeed the present results seem to point in entirely the opposite direction.

Sir J. J. Thomson (*Phil. Mag.*, 1924, [vi], 47, 337) recently advanced an expression for the velocity coefficient of a unimolecular reaction, namely,

$$k = \frac{Q}{R\theta} \cdot \frac{U_m}{\lambda} \cdot \epsilon^{-\frac{Q}{R\theta}},$$

based on the view that the immediate cause of chemical reaction is the interchange of energy due to molecular impact. If such is the case, it was argued that the introduction of an inert gas, for example argon, to the reaction chamber might be expected to exercise some influence on the velocity of decomposition. The present work was originally undertaken with this in view, and the decomposition of nitrogen pentoxide was chosen as the reaction to be studied, first, on account of its homogeneity and, secondly, on account of the convenience arising from the lowness of the temperatures which may be employed. A reinvestigation of the velocity and mechanism of the dissociation was first undertaken and the present paper embodies the main results obtained.

Preparation of the Nitrogen Pentoxide.—The substance was prepared as described by Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, 42, 1131). The method consists essentially of two processes, a distillation and a sublimation, and several modifications were made in the apparatus described in the above communication with a view to minimising the time necessary for the change over from the first to the second process. After a little practice it was found quite easy to obtain good yields of the pure white crystals of the pentoxide. These were stored in air-tight U-tubes, which, to prevent rapid decomposition of the substance, were immersed in ice and salt contained in a large Dewar vessel.

Apparatus.—The apparatus used for the actual determination of the velocity was similar in general outline to that used by Daniels and Johnston, although it differed in various details of construction. The following diagram represents the more essential features. Owing to the corrosive nature of nitrogen pentoxide, all parts of the apparatus with which it came into contact had to be entirely of

glass. As tap grease, a special preparation composed of liquid and solid paraffin was used and was found to be fairly resistant, though frequent renewals were necessary. The pressure gauge, G, used in these experiments was also constructed entirely of glass after the pattern described by Jackson (J., 1911, **99**, 1066), its action being similar to that of the well-known Bourdon type. The gauge actually used enabled a change in pressure of 0·5 mm. of mercury to be measured with considerable accuracy when a compensation method was employed, the actual readings being taken on a suitable mercury manometer.

Fig. 1.

Fig. 2.
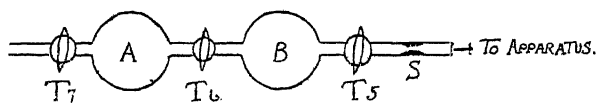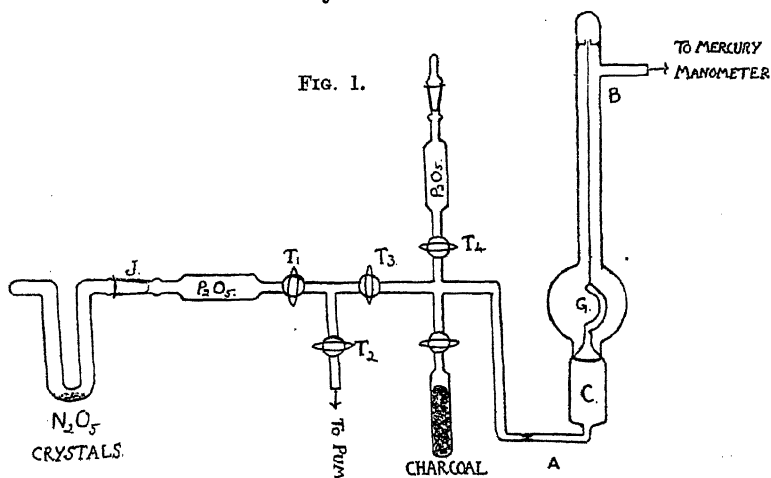
Experimental Procedure.—The whole apparatus to the right of tap T_1 was first evacuated with an oil-pump to a pressure of about 1 mm. of mercury. The final evacuation was then made by means of two liquid air–charcoal absorption tubes suitably situated. While the whole apparatus was thus evacuated, a zero reading of the glass fibre of the gauge was taken. Tap T_3 was then closed and the U-tube containing the pure pentoxide attached by the ground joint, J. The supernatant gases were pumped out two or three times to remove all traces of nitrogen tetroxide present, tap T_2 was closed, and the gaseous pentoxide allowed to pass into the reaction chamber, C, by means of taps T_1 and T_3. When approxi-

z 2

mately the desired pressure had been reached, the vessel was sealed off as rapidly as possible at A, a constriction having previously been made there to facilitate the sealing process. In cases where the effect of some foreign gas on the reaction velocity was being observed, this gas was introduced by means of tap T_4. After sealing, the vessel C was lowered into a large thermostat up to the point B. The variation in temperature of the thermostat did not exceed $\pm 0.01°$, whilst the actual temperatures themselves were obtained from three thermometers, previously calibrated by comparison with a thermometer recently standardised at the National

FIG. 3.
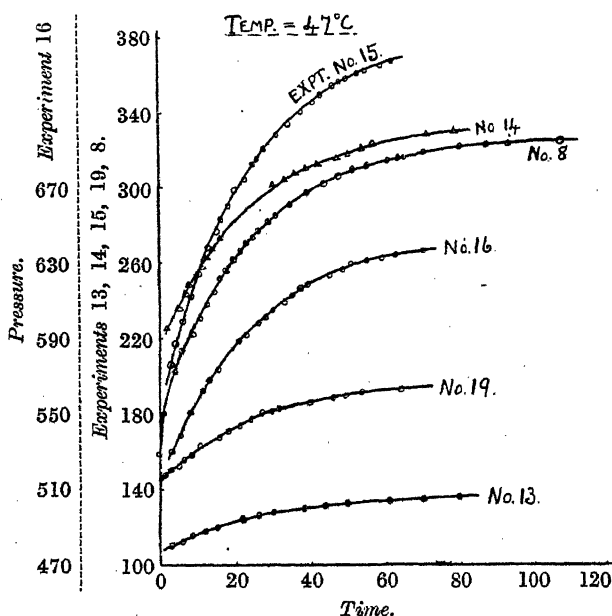
Physical Laboratory. The pressure in the outside compartment was then raised slightly and the time noted to within a few seconds when the fibre passed the zero point. The pressure was then read on the mercury manometer. All readings were corrected to $0°$. This process was repeated at frequent intervals, until the reaction was almost complete. The apparatus was then left for a considerable time, and a final observation taken, when the pressure became constant. Since the reaction is photosensitive, the whole experiment was carried out in a dark room. The illumination of the pointer and microscope scale was effected by a small, red lamp, which was only lit when an actual reading was taking place. Red light was

chosen on account of its photochemical non-activity, the experiments of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 72) having shown the active radiations to lie between the limits 460 $\mu\mu$ and 400 $\mu\mu$.

Calculation of Results.—The results were represented graphically as shown in Fig. 3, where, to save space, a selection of the curves obtained is given. The original scale used was large, 1 mm. being equivalent to 1 mm. of mercury in pressure. In the calculation of the reaction velocity coefficients, the pressure values were obtained from these curves by graphical interpolation for regular time intervals. The actual initial pressure of nitrogen pentoxide admitted was calculated in each case from the final constant pressure value. The neat, graphical methods of Daniels and Johnston (*J. Amer. Chem. Soc.*, 1921, **43**, 57) were exactly followed, but a short *résumé* of the necessary calculations is given here for easy reference. The decomposition of nitrogen pentoxide was assumed to take place according to the equation :

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$
$$\downarrow\uparrow$$
$$4NO_2$$
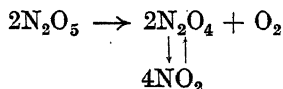
Owing to the alteration of the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium with change of partial pressure of the nitrogen tetroxide, a correction was rendered necessary. The following equations connect the various partial pressure components. When decomposition is complete, all the partial pressures being expressed in terms of that of oxygen,

$$P_f = 3P_{O_2} + 2\alpha P_{O_2},$$

where P_f is the final total pressure, P_{O_2} the partial pressure of the oxygen, and α the degree of dissociation of the nitrogen tetroxide. In the work of Daniels and Johnston, the degree of dissociation, α, was calculated from Schreber's equation, expressing the data obtained by Natanson. In the present calculations, the more recent equation given by Bodenstein (*Z. physikal. Chem.*, 1922, **100**, 78) was employed,

$$\log K = \log \frac{P_{N_2O_4}}{P^2_{NO_2}} = \frac{2891}{T} - 1.75 \log T - 0.0046T +$$
$$8.92 \times 10^{-6} T^2 - 6.8148.$$

Again, P_i, the initial pressure of nitrogen pentoxide, is obviously equal to $2P_{O_2}$.

Following the method of Daniels and Johnston, tables were constructed by giving arbitrary values to P_{O_2}, and the results embodied in large-scale graphs, whence the appropriate value of P_i could be obtained at once from the known experimental value of P_f.

Now, at any time during the reaction,

$$P = P_i + P_{O_2} + P_{N_2O_4} + P_{NO_2} - p,$$

where P is the observed pressure at time t, and p is the partial pressure that would be exerted by the pentoxide which has decomposed up to time t. Hence $P - P_i = P_{O_2} (1 + 2\alpha) = (\frac{1}{2} + \alpha) p$. Graphical interpolation was also employed to obtain the values of p, corresponding to experimentally determined values of $P - P_i$.

The formula for the velocity coefficient is then

$$k = \frac{2 \cdot 303}{t_2 - t_1} \log_{10} \frac{P_i - p_1}{P_i - p_2}.$$

Presentation of Results.—Table I gives the results of the calculations of the velocity coefficients from the experimental data for the decomposition of pure nitrogen pentoxide. The temperature was in all cases constant at 47°.

Experiments 2, 3, and 4 were conducted with a reaction chamber of approximate volume 25 c.c., experiment 8 in a chamber volume of 50 c.c., while in experiments 11 and 12 the vessel was packed with glass wool. The results obtained are in very good agreement among themselves, while their mean, $k = 37 \cdot 3 \times 10^{-3}$, agrees remarkably well with the calculated value, $38 \cdot 0 \times 10^{-3}$, obtained by use of the value of the critical increment deduced by Daniels and Johnston from their experiments. This was taken as 24,800 calories, and the value of k for 47° calculated by means of the equation

$$E = (1 \cdot 98 T_2 T_1 \times 2 \cdot 302 \log_{10} k_2/k_1)/T_2 - T_1,$$

where E is the critical increment and T_2 and T_1 are the absolute temperatures. The initial pressures in the above experiments were on the whole lower than those in the previous work, but it may be noted that the value of k obtained for the very low initial pressure in experiment 2, though slightly above the average, is still in good agreement. On the other hand, Daniels and Johnston found, for similar low initial pressures, values of k much above the average and Bodenstein (*Z. physikal. Chem.*, 1923, **104**, 51) has advanced a mechanism of the reaction at low pressures whereby such high values would be expected. If the correction he derives is applied to the above result, the value of k obtained is $32 \cdot 2 \times 10^{-3}$, which is now decidedly low. Indeed, this experiment by no means substantiates the theory of Bodenstein. This point, however, has not yet been further investigated.

The effect of argon on the velocity was next examined. Owing to the supposed autocatalytic nature of the reaction, the effect, if any, was not expected to be large. It seemed highly improbable, also, from a theoretical point of view, assuming reaction to be due to

TABLE I.

Experiment No. 2 ($P_i = 53.5$ mm.).

$t.$	$P.$	$P-P_i.$	$p.$	$k \times 10^3.$
10	79.8	26.3	19.4	—
20	91.0	37.5	28.0	29.2
30	100.0	46.5	35.8	36.5
40	106.2	52.7	41.8	30.6
50	111.1	57.6	45.2	47.1
60	114.0	60.5	48.1	43.0
70	115.5	62.0	50.0	43.3
—	—	—	—	—
—	—	—	—	—
Inf.	120.0	—	53.5	—
			Mean	38.3

No. 3 ($P_i = 121.5$ mm.).

$t.$	$P.$	$P-P_i.$	$p.$	$k \times 10^3.$
10	171.0	49.5	49.5	—
20	198.0	76.5	62.5	36.2
30	214.8	93.3	78.8	32.4
40	227.0	105.5	91.5	35.3
50	235.5	114.0	99.5	31.0
60	243.2	121.7	108.2	50.2
70	249.0	127.5	114.4	39.7
80	252.1	130.6	117.3	29.5
90	250.0	132.5	118.8	43.9
Inf.	257.5	—	121.5	—
			Mean	37.9

No. 4 ($P_i = 185.0$ mm.).

$t.$	$P.$	$P-P_i.$	$p.$	$k \times 10^3.$
10	257.0	72.0	58.4	—
20	297.2	112.2	98.2	37.8
30	321.3	136.3	122.0	32.1
40	337.5	152.5	139.9	33.4
50	349.5	164.5	152.4	32.5
60	358.8	173.8	163.0	39.6
70	364.5	179.5	169.7	36.3
80	368.2	183.2	173.0	24.4
90	371.4	186.4	177.5	46.9
100	373.8	188.8	180.2	44.6
—	—	—	—	—
—	—	—	—	—
—	—	—	—	—
—	—	—	—	—
Inf.	378.5	—	185.0	—
			Mean	36.4

No. 8 ($P_i = 157.6$ mm.).

$t.$	$P.$	$P-P_i.$	$p.$	$k \times 10^3.$
10	228.6	71.0	56.8	—
20	263.7	106.1	89.5	36.9
30	284.3	126.7	109.8	35.4
40	299.0	141.4	125.4	39.5
50	308.9	151.3	137.0	44.7
60	315.6	158.0	142.7	32.4
70	319.7	162.1	147.1	35.0
80	322.3	164.7	150.0	32.3
Inf.	329.2	—	157.6	—
15	247.8	90.2	73.7	—
25	274.8	117.2	100.8	39.1
35	292.3	134.7	118.0	36.0
45	304.4	146.8	130.9	39.4
55	312.3	154.7	139.4	38.3
65	318.0	160.4	145.5	40.7
			Mean	37.4

No. 11 ($P_i = 186.7$ mm.).

$t.$	$P.$	$P-P_i.$	$p.$	$k \times 10^3.$
10	275.2	88.5	73.2	—
20	313.0	126.3	109.3	38.3
30	335.3	148.6	132.6	35.8
40	350.8	164.1	149.2	36.6
50	361.2	174.5	160.5	35.9
60	369.3	182.6	169.3	40.9
70	374.1	187.4	174.5	43.9
Inf.	384.8	—	186.7	—
15	295.5	108.8	92.4	—
25	325.6	138.9	122.5	38.5
35	344.0	157.3	142.0	36.2
45	356.3	169.6	155.6	36.3
55	365.7	179.0	165.7	39.2
65	372.2	185.5	172.6	39.8
			Mean	38.3

No. 12 ($P_i = 195.3$ mm.).

$t.$	$P.$	$P-P_i.$	$p.$	$k \times 10^3.$
10	282.2	86.9	79.6	—
20	324.4	129.1	112.1	40.5
30	348.0	152.7	137.7	36.8
40	363.1	167.8	153.3	31.6
50	374.8	179.5	166.1	36.3
60	383.5	188.2	175.4	38.3
Inf.	400.8	—	195.3	—
15	305.5	110.2	93.8	—
25	337.4	142.1	126.0	38.1
35	356.0	160.7	145.6	33.2
45	369.5	174.2	160.1	34.6
55	379.7	184.4	171.2	37.9
65	386.0	190.7	178.4	35.5
			Mean	36.3

molecular impact, that any effect would be observed; for neither difference in the initial pressure of the pentoxide nor the actual gaseous products of the reaction gave rise to any measurable increase in the velocity. Both these factors would reduce the mean free path of the molecules, the volume of course remaining constant, and render collision more frequent. Since, however, as far as is known, this was the first case in which a rate of reaction had been

measured in an atmosphere of an inert gas, the experiments were carried through and the results are shown in Table II.

<div align="center">TABLE II.</div>

<div align="center">Experiment 5 ($P_t = 171·5$ mm.).</div>

<div align="center">Pressure of Argon admitted = 176·1 mm.   Temp. = 47°.</div>

t.	P.	$P-P_t$.	p.	$k \times 10^3$.
10	243·2	71·7	58·3	—
20	279·2	107·7	93·6	37·4
30	303·4	131·9	118·0	37·6
40	318·7	147·2	134·5	36·9
50	330·0	158·5	146·4	38·8
60	337·9	166·4	155·2	43·1
70	342·7	171·2	160·8	42·1
Inf.	354·6		171·5	

<div align="right">Mean 39·3</div>

<div align="center">No. 9 ($P_t = 101·0$ mm.).   No. 10 ($P_t = 115·5$ mm.).</div>

<div align="center">Pressure of Argon = 108·2 mm.   Pressure of Argon = 105·5 mm.</div>

t.	P.	$P-P_t$.	p.	$k \times 10^3$.	t.	P.	$P-P_t$.	p.	$k \times 10^3$.
10	154·4	53·4	41·1	—	10	179·5	64·0	50·2	—
20	173·5	72·5	58·0	33·2	20	201·7	86·2	70·1	36·3
30	188·4	87·4	71·2	36·7	30	216·5	101·0	84·3	37·5
40	197·6	96·6	80·0	35·0	40	226·7	111·2	95·0	42·0
50	203·5	102·5	85·5	30·4	50	233·8	118·3	101·8	40·3
60	207·8	106·8	90·3	36·1	60	238·0	122·5	106·0	36·6
70	210·8	109·8	93·4	35·1	70	240·2	125·7	109·0	37·9
Inf.	218·2	—	101·0	—	Inf.	247·8	—	115·5	—
15	164·3	63·3	49·7	—	15	192·2	76·7	61·7	—
25	181·4	80·4	65·2	36·2	25	209·8	94·3	77·8	35·6
35	193·5	92·5	76·0	35·6	35	222·0	106·5	90·0	39·1
45	200·8	99·8	83·0	32·8	45	230·4	114·9	98·6	41·1
55	206·0	105·0	88·3	34·9	55	236·2	120·7	104·1	39·4
65	209·5	108·5	92·1	35·4	65	239·1	123·6	107·9	40·5

<div align="center">Mean 34·7   Mean 38·7</div>

It will be seen that the above expectations were realised, as the mean of the values of k in the three experiments, namely, $k = 37·6 \times 10^{-3}$, is less than 1% higher than the previous value and well within the limits of experimental error. An inert gas, therefore, has no determinable effect on the velocity of this reaction, although it may be that, in this case, the catalytic effect outweighs all others.

Some doubts were entertained about the nature of this auto-catalysis, one ground being that the great increase in the concentration of nitrogen tetroxide during the course of the reaction did not give the slightest indication of an acceleration of the reaction. The effects of various other gases were therefore tried with a view to obtaining further evidence of the nature and mechanism of the reaction.

The effects of a large excess of the products of reaction were first examined. Three experiments were made with excess oxygen and

two with excess nitrogen tetroxide, but to save space the data of one only in each case are given in full in the following tables.

TABLE III.

Excess oxygen present.

Experiment 14 (Temperature = 47°).

Partial pressure of oxygen admitted = 123·5 mm.

t.	P.	$P-P_i$.	p.	$k \times 10$
10	254·4	93·0	76·5	—
20	282·0	120·6	104·6	40·2
30	300·4	139·0	122·5	37·9
40	310·3	148·9	133·1	31·9
50	318·5	157·1	141·9	38·2
Inf.	336·5	—	161·4	—
5	235·5	74·1	59·3	—
15–	269·8	108·4	92·0	38·6
35	305·7	144·3	128·4	37·7
45	314·4	153·0	137·9	34·0
55	322·0	160·6	145·5	39·1
			Mean	37·2

Expt.	P_i.	P_{O_2} (original).	$k \times 10^3$.
13	60·6	122·8	38·3
15	187·0	163·0	35·9

TABLE IV.

Excess nitrogen tetroxide present.

Experiment 16 (Temperature = 47°).

Pressure of equilibrium mixture of dioxide and tetroxide admitted = 227·5 mm. at 17·2°.

t.	P (total).	$P-P_i$.	p.	$k \times 10^3$.
10	558·3	373·8	72·5	—
20	586·2	401·7	106·6	36·3
30	605·3	420·8	130·2	36·1
40	618·6	434·1	146·2	35·0
50	627·2	442·7	157·9	36·4
60	632·9	448·4	165·1	31·6
Inf.	647·5	—	184·5	—
5	536·7	352·2	47·0	—
15	573·5	389·0	91·2	38·8
25	596·4	411·9	119·2	35·7
35	612·2	427·7	139·0	36·2
45	623·4	438·9	153·1	37·1
55	630·3	445·8	161·9	33·0

Experiment 16 : Mean value $k = 35·6 \times 10^{-3}$.
Experiment 17 : Mean value $k = 36·7 \times 10^{-3}$.

Owing to the continuous alteration of the $N_2O_4 \rightleftarrows 2NO_2$ equilibrium, considerable modification had to be made in the calculation of the results of experiments 16 and 17. Thus, if P_x is the pressure of the equilibrium mixture of dioxide and tetroxide introduced, from a knowledge of K, the equilibrium constant at the temperature

z*

in question, it is possible to calculate the pressure, P_M, the gas would exert if it were all present as pure tetroxide.   For

$$P_x = (1 + \alpha)P_M, \text{ while } K = P_{N_2O_4}/P^2_{NO_2} = (1 - \alpha)/(4\alpha^2 P_M)$$

and therefore $4KP^2_M - (8KP_x + 2)P_M + (4KP_x + 1)P_x = 0$ (1)

From this equation P_M can be obtained.

To calculate P_i, the new equations will be

$$P_f = P_{N_2O_4} + P_{NO_2} + P_{O_2} + P^1_{N_2O_4} + P^1_{NO_2},$$

where $P^1_{N_2O_4}$ and $P^1_{NO_2}$ are the respective partial pressures of tetroxide and dioxide in the admitted mixture.

Hence $P_f = 2(1-\alpha)P_{O_2} + 4\alpha P_{O_2} + P_{O_2} + (1 - \alpha)P_M + 2\alpha P_M$
          $= \frac{1}{2}(3 + 2\alpha)P_i + (1 + \alpha)P_M$, since $P_i = 2P_{O_2}$.   (2)

Now $K = \dfrac{P_{N_2O_4} + P^1_{N_2O_4}}{(P_{NO_2} + P^1_{NO_2})^2} = \dfrac{2P_{O_2}(1 - \alpha) + P_M(1 - \alpha)}{(4P_{O_2} + 2\alpha P_M)^2}$

i.e., $K = \dfrac{(1 - \alpha)}{4\alpha^2(2\overline{P_{O_2} + P_M})}$ . . . .   (3)

By elimination we obtain

$$\alpha^2(4KP_M + 8KP_f + 2) + \alpha - 3 = 0,$$

α being determined, P_i is then obtained from equation 2.

In the same way it can be shown that

$$P - P_i = (\tfrac{1}{2} + \alpha)p + (1 + \alpha)P_M . . .   (4)$$

whence, by use of equation 3,

$$\alpha^2(4KP_M - 8K\overline{P - P_i} - 2) + \alpha + 1 = 0 . . (5)$$

Equations 4 and 5 enable the values of p to be determined and then the calculation is as before.

The actual mean values of k finally obtained, $37 \cdot 1 \times 10^{-3}$ in the case of oxygen excess and $35 \cdot 6 \times 10^{-3}$ in that of the tetroxide, are in very good agreement with the previous experimental data. The value in the case of the tetroxide is slightly lower, but owing to increased difficulty of manipulation the margin of experimental error is also correspondingly increased.

The effect of dry air was next examined, and the value of k obtained (Experiment 18, $k = 37 \cdot 5 \times 10^{-3}$) also showed no deviation from the previous results. The possibility of impurities such as nitrogen and carbon dioxide exercising a ruling effect on the progress of the reaction was thus put out of the question.

It was considered of interest to examine, also, the effect of moist air, and in Experiment 19 air was admitted straight into the reaction chamber without any preliminary drying or purification. As the value of k obtained seemed rather remarkable, the results are shown in full in Table V.

TABLE V.

Experiment 19 (Temperature = 47°).

Pressure of air admitted = 122·3 mm.

$t.$	$P.$	$P - P_t.$	$p.$	$k \times 10^3.$
10	159·8	69·0	54·7	—
20	172·7	81·9	66·3	39·3
30	181·2	90·4	74·0	37·7
40	186·2	95·4	78·9	34·5
50	190·0	99·2	82·5	36·0
Inf.	198·5	—	90·8	—
5	152·3	61·5	48·0	—
15	166·6	75·8	60·6	34·9
25	177·6	86·8	70·6	40·2
35	183·9	93·1	76·5	34·6
45	188·1	97·3	80·7	34·7
				Mean 36·5

When this experiment was undertaken, it was quite expected that the water vapour present would exercise a considerable disturbing effect on the velocity of decomposition, on account of the occurrence of the secondary reaction, $H_2O + N_2O_5 \longrightarrow 2HNO_3$, and on account of the pronounced polarity of the water molecule. On the contrary the velocity of reaction is still unchanged. A possible explanation may lie in the method of calculation of the initial pressure of the pentoxide. The water molecules present would react instantaneously with the nitrogen pentoxide molecules to give nitric acid, after which the dissociation would proceed. The initial pressure of pentoxide calculated would then of necessity be the pressure after this preliminary reaction. Since this initial combination would take place in a shorter time than it took to admit and measure the pressure of the air, it could not be detected on the present apparatus. In any case, however, in this experiment small traces of nitric acid not present in other cases must have been in the reaction vessel during the actual measurements of the rate of decomposition. If then, as seems most likely, the molecules of the acid formed some sort of surface layer on the walls of the vessel, there is obviously here a further argument in favour of the true homogeneity of this reaction.

In order to complete the investigation experiments were performed at a lower temperature with a view to determine the temperature coefficient. The data of two such experiments are summarised in the following table.

TABLE VI.

Temperature = 35·4°.

Expt.	$P_f.$	$P_i.$	$k \times 10^3.$
21	320·0	172·6	6·82
23	300·2	165·3	7·40
		Mean	7·11

z* 2

The value calculated for the same temperature from the data of Daniels and Johnston, namely, $k = 7 \cdot 71 \times 10^{-3}$, is seen to be very close to the above mean value. The extremely large value of the temperature coefficient, namely, an increase of over 300% in the velocity for a 10° rise in temperature, seems to afford additional evidence in support of the view that catalysis by the walls of the vessel is not a factor in determining the reaction velocity.

In the next series of experiments undertaken, an attempt was made to repeat the results of Daniels, Wulf, and Karrer (*loc. cit.*). On this work had been based their conclusion that the nitrogen tetroxide is the autocatalytic agent in the reaction. They had found that the initial rate of decomposition of the pentoxide when perfectly free from all traces of tetroxide was extremely slow. The complete elimination of nitrogen tetroxide was ensured by the presence of a small excess of ozone, and the appearance of brown fumes due to the commencement of the dissociation of the pentoxide was then watched for. The results of one experiment only are quoted, and in this case the gaseous pentoxide was kept for 280 minutes before the brown coloration was noted, during 75 minutes of which time the temperature of the vessel was maintained at 80°. It can be calculated that at this temperature the brown fumes should have appeared in about 0·002 second, assuming the decomposition of the pentoxide to take place in accordance with the results of Daniels and Johnston (*loc. cit.*).

In the first case a qualitative experiment was made on the same lines as before, with the difference that now dry ozonised oxygen was admitted. The ozone content of the mixture was in all the following cases between 3 and 3·5% by volume and was measured in the usual manner by absorption in neutral potassium iodide solution, acidification, and subsequent titration with sodium thiosulphate solution. Since the oxidation of nitrogen tetroxide to nitrogen pentoxide by ozone is instantaneous (Wulf, Daniels, and Karrer, *loc. cit.*, p. 2398), the admission of excess ozone ensured the presence of pure pentoxide only and consequently it was expected to find a definite point of inflection on the velocity curve, where the pentoxide began to decompose uniformly. No such effect was observed, all the points lying on a perfectly smooth curve. As this was the case, colorimetric determinations were undertaken similar in nature to those of the above authors, the main difference being that here the starting point was nitrogen pentoxide with a very small percentage of tetroxide present, instead of pure tetroxide. The results of several such determinations are presented in Table VII.

A spectroscopic method of determining the first appearance of the

TABLE VII.

No. 1. Pressure of N_2O_5 = 31·5 mm. Pressure of ozone–oxygen mixture = 519·0 mm.			No. 3. Pressure of N_2O_5 = 38·5 mm. Pressure of O_3–O_2 mixture = 469·0 mm.		
Time (min.).	Temp.	Colour.	Time (min.).	Temp.	Colour.
0	15°	Colourless.	0	20°	Colourless.
75	15	Colourless.	75	20	Colourless.
80	Immersed in thermostat, at 47		79	Heated to 47	—
90	47	Trace of colour.	81	47	Dense brown.
100	47	Dense brown.			

No.	Temp.	$P(N_2O_5)$.	$P(O_3$–O_2 mixture).	Time of colour change.
·2	47°	64·0 mm.	469·0	After 3 min.
5	60	47·5 ,,	308·5	Instantaneous.
6	20	47·0 ,,	308·5	After 160—170 min.
7	33	52·0 ,,	410·0	After 9 min.
8	35	23·5 ,,	215·0	After 7 min.

nitrogen tetroxide was tried, but direct vision by the naked eye of the vessel suitably illuminated was found to be quite as sensitive. It will be seen that in no experiment was the effect noted by Daniels, Wulf, and Karrer observed. The appearance of the brown fumes at 80° was to all intents and purposes instantaneous in every case, whilst, wherever tested, the rate of pressure increase was found to be uniformly smooth.

An endeavour to substantiate the accuracy of the above results proved entirely successful. This was done in the following manner. A system of bulbs as shown in diagram 2 was attached to the apparatus. The whole was first carefully evacuated, tap T_6 was then closed, and the pentoxide admitted to a known pressure. A large excess of ozonised oxygen was then allowed to flow in and the final pressure noted. Any tetroxide present would at once be oxidised to pentoxide. Tap T_5 was then closed and the tube quickly sealed at S and drawn off. An estimation of the excess ozone in bulb B was immediately carried out. After absorption of the nitrogen pentoxide in water, the remaining gases were driven into bulb A, where the ozone content could be measured in the usual manner. From a knowledge of the volume of bulb B, and of the actual amount of ozone present, the partial pressure of the ozone in the mixture could be calculated, and hence the concentration of the excess ozone in the actual vessel wherein the coloration experiment was being conducted could be determined.

In the first case investigated, the actual amount of ozone determined was 0·00072 g. The volume of the bulb was 94 c.c., whence the partial pressure of the excess ozone is found to be 2·72 mm. Now, assuming the reaction proceeds unhindered by ozone and neg-

lecting the decomposition of the ozone itself, a calculation can be made of the time which must elapse before the appearance of the brown fumes. The time required for the decomposition of the excess ozone on the assumption that it is continuously oxidising the tetroxide that is formed is given by

$$t = P_{O_3}/k \cdot P_{N_2O_5},$$

where k is the velocity coefficient of the decay of nitrogen pentoxide at the temperature in question. Two accurate coloration experiments were conducted with the above excess of ozone, the first at 47°, the second at 18·5°, and the times that elapsed before the appearance of the brown colour due to free tetroxide were 2 min. and 95 min. respectively. From the known initial concentration of ozone in the inflowing ozonised oxygen, the amount of tetroxide present as impurity in the nitrogen pentoxide was calculated and hence the true initial pressure of the pentoxide was found to be 35 mm.

From the above formula,

at 47°, $t = 2\cdot72/35 \times 0\cdot037 = 2\cdot1$ min.
while at 20°, $t = 2\cdot72/35 \times 0\cdot0008 =$ approx. 97 min.

Two other similar experiments were conducted, both giving entirely concordant results. It may be mentioned that in one case where the partial pressure of the excess ozone was 28·2 mm. and the initial pressure of nitrogen pentoxide only 37 mm., whilst no colour change was observed after 92 min. at 19°, on raising the temperature suddenly to 80°, the change was immediate. The same type of calculation may be applied to all the previous results contained in Table VII, although only approximate answers can be obtained, since the concentration of the excess ozone was by no means accurately known. No obvious disagreement will, however, be found in any of the cases examined.

An explanation of the effect observed by Wulf, Daniels, and Karrer (*loc. cit.*) has been sought, but so far with no success. Since extreme care was taken both in the preparation of the nitrogen pentoxide and in the purification of the oxygen, as well as in the drying of these gases, the possibility of the presence of some positive catalyst in the present experiments which was lacking in those of the above-mentioned authors seems extremely remote. The question of the presence of water vapour might be raised, but to ensure its absence as far as possible in every case the reaction bulb was baked out under vacuum and all the entering gases were passed through phosphorus pentoxide drying tubes. Consequently the only water vapour which could have been present must have been that left in

the walls of the reaction vessel, since the removal of every trace from the glass is an extremely difficult matter. Wall effect, however, seems not to be a factor, in so far as the variation of surface area can be regarded as a true criterion of its absence, so it would not be expected that any such residual traces left in the walls would affect the course of the reaction. The large temperature coefficient, found both in the former and in the present work, also lends support to the view that the velocity of a true chemical reaction is being measured. Indeed, in view of the above results, in the case of the thermal decomposition of nitrogen pentoxide, evidence in support of the autocatalysis by traces of nitrogen tetroxide is entirely lacking. All the data now available seem to render more than probable the assumption that this reaction is really homogeneous and non-catalytic. Some importance may also be attached to the fact that no inhibitor of the reaction has yet been found. Indeed, the constancy of the values of k under very different conditions seems remarkable in the extreme.

If it is correct to assume the absence of any autocatalytic effect, an assumption which seems to be well supported by the experimental data, questions of great interest arise as to the mechanism of the reaction. What, for example, is the primary cause of the activation of the molecules and how is the supply of active molecules then maintained? Is it a kinetic collision effect as postulated in the " hot molecule " theory of Christiansen and Kramers (loc. cit.), or is there communication of energy by collisions of the second kind as in the phenomena recently described in the work of Cario and Franck (Z. Physik, 1922, 11, 161)? It is hoped that considerable information on these lines may be obtained from a study of the reaction velocity at low pressures, where the mean free path of the molecules is large. Investigations of this nature are now being conducted in collaboration with Dr. Rideal.

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XCVI.—*Limits for the Propagation of Flame in Inflammable Gas–Air Mixtures. Part III. The Effect of Temperature on the Limits.*

By ALBERT GREVILLE WHITE.

In many industrial processes inflammable gas–air mixtures are used at elevated temperatures. A knowledge of the effect of initial temperature on the limits for the propagation of flame in gas–air mixtures is thus of importance, and this work was initiated partly to procure such knowledge, and partly in an attempt to secure some information as to the mode of propagation of flame in limit mixtures.

Since a flame travelling along a tube containing an inflammable gas mixture must bring each layer in turn to a temperature at which it can burn, the ignition temperature of a gas might be expected to affect materially the limiting quantities which could be mixed with air to give a mixture which will propagate flame. Bunsen, in his "Gasometriche Methoden," attempted to deduce certain ignition temperatures from determinations of limits for the propagation of flame on the assumptions that the heat liberated in the burning layer is all transferred to the next unburnt layer, and is just sufficient to raise the latter to its ignition temperature. Ignition temperatures experimentally determined differed considerably from Bunsen's values, and more recent attempts to calculate limits from ignition temperatures on similar lines have also proved unsatisfactory, as may be seen from the figures given in Table I. The lower-limit values there given were determined for downward propagation (Part I and J., 1922, **121**, 1244), in order to eliminate convection effects as far as possible.

TABLE I.

Limits for the propagation of flame in various combustible–air mixtures.

Combustible.	Net calorific value.	Ignition temp.	Lower limit. Expt. (E).	Calc. (C).	$R = E/C$.
Methane	190	700°	5·95	2·55	2·3
Hydrogen	57	585	8·8	6·9	1·28
Ethyl ether	604	227	1·85	0·235	7·9
Carbon monoxide ...	68	651	15·3	6·5	2·35
Acetylene	301	429	2·78	0·94	3·0
Ethylene	315	543	3·33	1·16	2·9

The values used for the specific heats of methane, ether, acetylene, and ethylene were 15·2, 31·7, 11·5 and 13·0 Cals. respectively. For nitrogen, carbon dioxide, and steam, the values were those of

Holborn and Henning (*Ann. Phys.*, 1905, [iv], **18**, 739; 1907, [iv], **23**, 809), whilst for the other gases those of Lewis and Randall (*J. Amer. Chem. Soc.*, 1912, **34**, 1128) were taken. All the figures were for constant pressure and no correction has been made for loss of heat. The ignition temperatures used are those of Dixon and Coward (J., 1909, **95**, 514), except for ether, for which the mean value given by Tizard and Pye (*Phil. Mag.*, 1922, [vi], **44**, 79) has been utilised.

The large ratios of the two limits in Table I suggest that only a small part of the heat given out by a burning layer is used to heat the next layer to its ignition temperature, whilst the variations in the ratios indicate that the percentage so used differs greatly for different combustibles. The heat not so used may be lost (1) to the tube containing the gas, (2) to the bulk of the unburnt gas, (3) to the burnt gas; but in most cases there would appear to be much more heat left than would be necessary to raise the unburnt layer to its ignition temperature. The great conductivity for heat of hydrogen might be advanced to account for the low value of the ratio in this case, but in the other cases, where the conductivities of the lower-limit mixtures, and the calorific values per unit volume, should not differ much, the flame temperatures, the heat losses, and the rate at which the heat is transmitted to the nearest unburnt layer should be similar, so that there should be a rough parallelism between the ignition temperatures and the calorific values at the lower limit. Since this is not the case, it appears that the ignition temperature of the gas has little direct connexion with the propagation of flame in the lower-limit mixture, and that the effective ignition temperature during the propagation of flame may often be much greater than that ordinarily determined (compare J., 1922, **121**, 1244).

The question is obviously important. A simple method of procuring information appeared to be that of determining the limits of gas mixtures at various temperatures. The method depends on the assumption that the ignition temperature of a gas mixture at concentrations similar to those present in a lower-limit mixture does not vary much with the concentration of the inflammable gas. This assumption has not been proved to hold generally, but it has been shown to hold for hydrogen–oxygen mixtures by Dixon and Crofts (J., 1914, **105**, 2036), and for methane–air mixtures by Wheeler (*Trans. Inst. Mining Eng.*, **63**, Part I, 14), whilst Tizard and Pye (*loc. cit.*) believe that the ignition temperature changes little throughout the whole range for heptane–air. If the ignition temperature functioning during propagation were high, the change to be expected in the limit when the initial temperature of the gas

mixture is changed by a definite amount would be less than if the ignition temperature were low.

Published Information Available.—The amount of work that has been carried out on the effect of the initial temperature of a gas–air mixture on its limits for the propagation of flame is comparatively small, and the main portion deals only with methane–air mixtures. The communications dealing with the subject in any detail are referred to below.

Author.	Reference.	Mixtures considered.
Bunte and Roszkowski. Roszkowski.	*J. Gas Wasser.*, 1890, 491, 524, 535, 553. *Z. physikal. Chem.*, 1891, **7**, 485.	Methane, hydrogen, carbon monoxide and illuminating gas with oxygen, air and an artificial atmosphere.
Le Chatelier and Boudouard.	*Compt. rend.*, 1898, **126**, 1344.	Carbon monoxide and air.
Taffanel and Le Floch.	*Ibid.*, 1913, **157**, 595.	Methane and air.
Burrell and Robertson.	U.S. Bureau of Mines, Tech. Paper 121, 1916.	Methane and air.
Mason and Wheeler.	J., 1918, **113**, 45.	Methane and air.
White.	J., 1922, **121**, 1688.	Ammonia with air and oxygen.
Berl and Fischer.	*Z. Elektrochem.*, 1924, **30**, 29.	Carbon monoxide, hydrogen, methane, acetylene, ethylene, and certain organic vapours with air.

The most ambitious of the older programmes was attempted by Bunte and Roszkowski, who made use of a small vessel. Their results would tend to show that in many cases the limits change little when the initial temperature of the gas is varied from 15° to 300°. This is not a result to be expected on theoretical grounds, and is almost certainly due to a change in the composition of the gas mixture due to an over-long preliminary heating.

The experiments of Le Chatelier and Boudouard were carried out in a tube, and showed that there was an important change in the limit of carbon monoxide–air when the initial temperature was increased. Taffanel and Le Floch, and also Mason and Wheeler, used a tube. The dimensions are not given by the earlier workers but that used by Mason and Wheeler was 20 mm. in diameter and 15 cm. long. The English workers dealt with propagation downwards, but allowed the flame to travel up a vertical limb connected to the bottom of the limit tube proper in order to ascertain easily when propagation occurred. Burrell and Robertson used as limit vessel an explosion pipette, and decided whether the mixture was above or below the limit by analysing the gas left in the pipette after sparking.

The author's work with ammonia mixtures was carried out

with tubes considerably larger than most of those previously utilised for such experiments, the object being to obtain more accurate results. The work recently published by Berl and Fischer is said to be on explosion limits, and the experimental conditions were not conducive to accurate work on limits for the propagation of flame. The explosion vessel was a glass pipette of unspecified dimensions, but was small enough for a powerful spark to give limit results markedly different from those given by normal spark-ing. Two sets of results were taken at each temperature, the mixture remaining in the heated pipette for 1 minute in the one series, and for 2 minutes in the other, before firing. The results were in agreement over the whole temperature range only for hydrogen and methane at both limits, and for acetone at the lower limit; definite results were not obtained for either acetylene or ethylene at the upper limit. The lack of agreement between the two sets of results for carbon monoxide, ethylene, and acetylene indicates that preliminary combustion of these mixtures took place during the second minute, so that the results given for these gases for 1 minute's heating should be regarded with suspicion.

EXPERIMENTAL.

The method previously utilised for ammonia was employed, and the aim was accuracy at moderate temperatures rather than less trustworthy results at higher temperatures. As there was con-siderably more danger of " baking " with the gases now used than with ammonia, the heating of the gas mixtures was speeded up by using a tube 25 mm. in diameter. The tube was of the same length as before — 1·5 metres. Except where otherwise specified, the experimental details were precisely as previously described. An accuracy of 1% on the inflammable gas used was aimed at. All the results are for downward propagation, except where otherwise specified.

To obtain more uniform heating near the ends of the furnace than was possible during the former experiments, special auxiliary heating coils were wound. These proved quite successful, and reduced the variation of temperature along the furnace from 20° to less than 10° at the highest temperature used. The gas mixture was made up in a 6-litre glass aspirator, and the amount of mercury introduced into this before filling the tube from it was carefully adjusted, so that there should be no excess of pressure over that of the atmosphere when once the gas in the tube had attained the furnace temperature. This was done by preliminary trial, as a small portion of the tube projected from the furnace and was thus at a temperature that was not known accurately. A very large

TABLE II.

Showing the ranges that will propagate flame at various temperatures for mixtures of various gases with air in tubes 25 mm. in diameter, and also the results of determinations for methane in tubes 18 mm. in diameter.

Ranges that will propagate flame in

Temp.	H₂.	CO.	CH₄. 25 mm.	CH₄. 18 mm.	C₂H₄.	C₂H₂.	n-C₅H₁₂.
17°±3°	9·40 to 71·5	16·3 to 70·0	6·30 to 12·9	— to 12·7	3·45 to 13·7	2·90 to 55·0	1·53 to 4·50
50	9·2 to —	15·7 to —	6·20 to —	— to —	3·35 to —	2·83 to 59·0	1·50 to —
100	8·8 to 73·5	14·8 to 71·5	5·95 to 13·7	— to 13·3	3·20 to 14·1	2·68 to 65·0	1·44 to 4·75
150	8·3 to —	14·2 to —	5·75 to 14·1	— to —	3·10 to —	2·52 to 73·0	1·39 to 4·90
200	7·9 to 76·0	13·5 to 73·0	5·50 to 14·6	— to 14·1	2·95 to 14·9	2·39 to 81·0 *	1·34 to 5·05
250	7·5 to —	12·9 to —	5·30 to —	— to —	2·85 to 15·7	2·30 to —	1·30 to —
300	7·1 to 79·0	12·4 to 75·0	5·10 to 15·5	— to 15·0	2·75 to 17·9	2·19 to —	1·22 to 5·35
350	6·7 to —	12·0 to —	4·90 to —	— to —	2·60 to —		
400	6·3 to 81·5	11·4 to 77·5	4·80 to 16·6	— to 15·8	2·50 to —		
450			4·55 to				

* This value is known to be somewhat low, but was the highest value obtainable under the experimental conditions. For this result, the gas mixture was in the tube 2 seconds before ignition. Allowing the gas mixture to remain an extra 2 seconds in the tube before ignition gave a still lower figure for the limit.

stopcock was introduced between the tube and the bottle, so that the filling of the tube occupied the minimum of time. The time between the opening of the cock and the firing of the mixture was finally reduced to a little over 2 seconds. Whenever there was any doubt as to the condition of a mixture at the time of firing, the result was checked by firing the same mixture, allowing it to remain an extra 2 seconds in the tube before ignition. The thermocouple was removed from the tube immediately before firing, but another couple, placed between the tube and the furnace wall, registered

any change occurring later. The result of a trial was determined visually through an observation hole in the asbestos packing at one end of the tube. Owing to the distance between the tube and the wall of the furnace, after practice it was comparatively easy to follow the progress of a flame down the tube.

The inflammable gases used were prepared as described in Part I.

FIG. 1.

Showing the lower-limit values for the propagation of flame in methane–air mixtures obtained by various workers. No curve is drawn through the results of Taffanel and Le Floch, which are shown by asterisks.

I *Mason and Wheeler.* II *Burrell and Robertson.* III *White.* IV *Roszkowski.* V *Berl and Fischer.*

As previously noted with ammonia–air, whenever preliminary "baking" of a mixture took place at a certain temperature, the effect was far more serious at the upper than at the lower limit. All percentages quoted are percentages by volume.

Results.—The results obtained are given in Table II.

A comparison of the author's results with those of other workers is best made by means of Figs. 1 to 4. From the point of view of such a comparison, the absolute value obtained for the limit

at the ordinary temperature is of little account, and it is the slope and general form of the curves that are important. The lower-limit results obtainable for methane (Fig. 1) show that the values of Roszkowski and of Berl and Fischer, who used small vessels and prolonged heating of the gas mixture, indicate a very much smaller fall in the value of the limit with rise of temperature than the results of the other workers. The results of Roszkowski even

FIG. 2.

Showing the upper-limit results for the propagation of flame in methane-air mixtures determined by various workers.

Percentage of methane present at the upper limit.
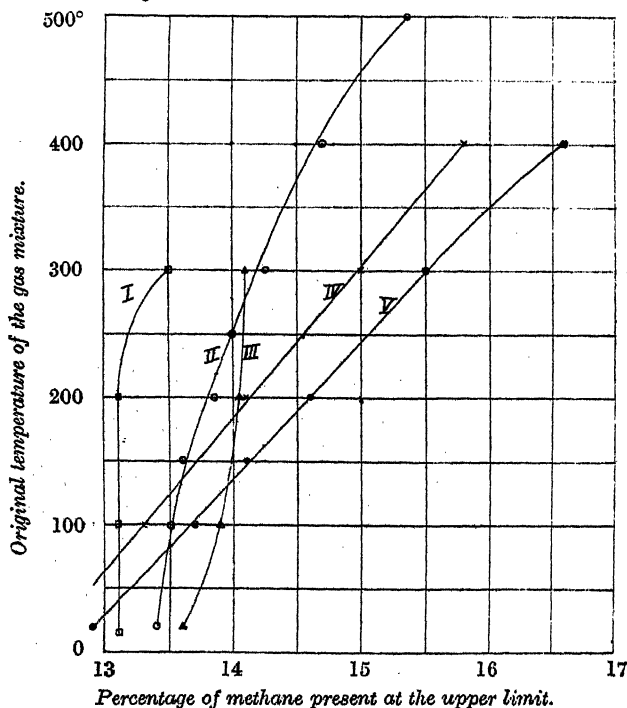
I *Roszkowski.*   II *Mason and Wheeler.*   III *Berl and Fischer.*   IV *White 18 mm.*   V *White 25 mm.*

indicate an increase in the value of the limit when the temperature of the gas mixture is increased from 100° to 300°, and it is certain that both sets of results are in error. The results of Taffanel, of Mason and Wheeler, and of Burrell and Robertson all agree fairly well. The author's results, lying along a straight line, might almost be the mean of those of the American and the English observers. The upper-limit results (Fig. 2) differ considerably from one observer to another. The results of Roszkowski and of Berl and

Fischer, regarded as limits for the propagation of flame, again appear to be at fault, as the relative values of some of their figures are improbable in the extreme. There is in this case a serious

FIGS. 3, 4, 5, 6.

Showing the results of various workers for the effect of temperature on the limits of carbon monoxide, hydrogen, acetylene, and ethylene when mixed with air.

The results of Le Chatelier and Boudouard for carbon monoxide are shown by asterisks. The dotted curves for Berl and Fischer show results of experiments in which the mixture was kept at the required temperature for 2 minutes, instead of the usual 1 minute.

R = Roszkowski.   B = Berl and Fischer.   W = White.

3.—Carbon Monoxide.
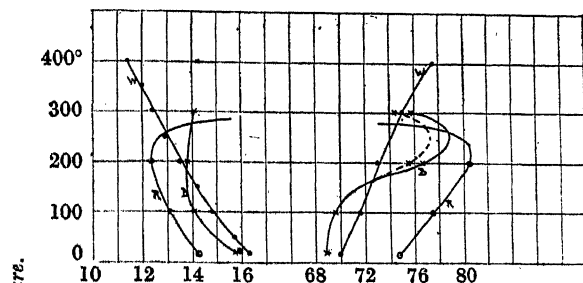
4.—Hydrogen.

5.—Acetylene.   6.—Ethylene.

Percentage of combustible needed to give a limit mixture.
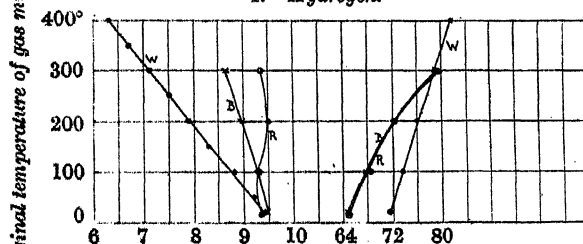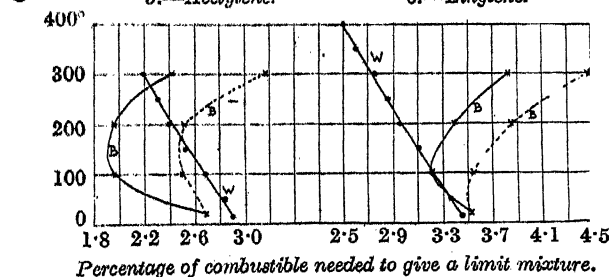
discrepancy between the values now found and those of Mason and Wheeler, as when the initial temperature of the gas mixture is changed from about 20° to 400°, the percentage increase is in

one case about three times that in the other. As the limit vessel used by Mason and Wheeler for their experiments was only 20 mm. in diameter, further determinations were made in a tube having an internal diameter of 18 mm., but a length of 1·5 metres. The slope of the temperature–limit curve is decreased by decreasing the diameter of the tube used as limit vessel, but the effect of diameter alone is not sufficient to account for the difference between the two sets of results. Under the conditions used in this work, horizontal propagation gives results differing only slightly from those for downward propagation. Thus the upper limit for methane in air increased from 12·9 to 15·7% for horizontal propagation when the initial temperature of the mixture was increased from 18° to 300°. The increase in the limit for downward propagation under the same conditions was from 12·9 to 15·5%.

Figs. 3—6 show the present results in comparison with those of Berl and Fischer, Roszkowski, and of Le Chatelier and Boudouard. In no single case do the older results agree with those now determined, and in only one instance, that of the upper limit for hydrogen, can any two sets of them be said to agree amongst themselves. Such discrepancies would not be surprising at very high temperatures, but here they are often large for results between 15° and 100°.

Discussion of Results.

At the lower limit, for all gases except carbon monoxide the present results give straight lines for the temperature–limit curve, and even for this gas the departure from the linear form is not great. At the upper limit the same thing is nearly true, except for ethylene and acetylene, for which the limits increase very rapidly at higher temperatures. Mason and Wheeler observed a similar phenomenon in the case of methane at high temperatures. They seemed to think that at the higher temperatures the results obtained did not properly represent the upper limit for self-propagation in *methane* and air, and suggested the possibility of the early formation of carbon monoxide and hydrogen (both gases having very high upper limits of inflammability). To test this theory, the author exposed ethylene upper-limit mixtures to a high temperature in limit tubes for various short times. The results were not quite conclusive, but did not seem to support this explanation of the high limit results. The difference observed with carbon monoxide at 400° is much too small to settle the question, as these upper-limit results were only decided to the nearest 0·5%. Experiments with this gas at higher temperatures might enable a decision to be made, as it certainly cannot give rise to any known compounds except carbon dioxide under the experimental conditions obtaining.

It has been shown (J., 1922, **121**, 1688) that at the lower limit in ammonia–air and –oxygen mixtures the theoretical flame temperature remains practically constant for a range extending from the ordinary temperature to 450°. The same calculations have been made for the gases now examined. The results given in Table III show that in all but two cases the theoretical flame temperature remains much the same throughout the temperature range utilised. There appears to be some slight tendency for the flame temperature to decrease as the initial temperature of the mixture is increased, but this increase is little greater than the experimental variations. Of the two exceptions, one is only an exception below 100°—at and above that temperature the results for carbon monoxide agree with those for the majority. In the case of hydrogen, however, the flame temperature increases steadily with the initial temperature, the increase over the whole range being far outside any possible manipulative experimental error. We thus see that at the lower limit the results for six out of the seven gases examined conform approximately to a simple rule, so that from the practical point of view it becomes easy to make an allowance for the effect of temperature on the lower limit. Of its significance on the theoretical side it need only be said that, once granted the required premises as to the rate of variation of the ignition temperature near the lower limit, it appears to do away with any idea that the ordinary ignition temperature of a gas can have any direct connexion with the propagation of flame in it.

TABLE III.

Showing the theoretical flame temperatures attained at the lower limit, and in some cases at the upper limit, for the propagation of flame in various gas–air mixtures at different temperatures up to 450°.

Theoretical flame temperature.

Initial temp. of gas mixture.	Hydrogen. Lower limit.	Upper limit.	Carbon monoxide. Lower limit.	Upper limit.	Methane. Lower limit.	Ethylene. Lower limit.	Acetylene. Lower limit.	n-Pentane. Lower limit.
17°±3°	815°	980°	1490°	1120°	1535°	1420°	1195°	1490°
50	820		1465		1530	1405	1195	1475
100	825	970	1435	1130	1515	1390	1180	1475
150	830		1425		1515	1395	1165	1475
200	845	975	1410	1160	1505	1385	1160	1475
250	860		1405		1505	1390	1170	1485
300	875	970	1405	1170	1505	1400	1175	1465
350	890		1415		1505	1390		
400	900	980	1410	1170	1530	1395		
450					1520			

The upper-limit results show that of the two gases available for calculation one agrees with ammonia in showing a theoretical flame

temperature that increases with increase of initial gas temperature, whilst the other shows almost identical flame temperatures under the same conditions.   Owing to our ignorance of the exact products of combustion at the upper limit, in many cases it is not possible to find out how the theoretical flame temperature or calorific value at this limit is affected by rise of temperature of the original mixture.   For upper-limit results, therefore, Fig. 7 has been drawn, showing how the oxygen–combustible ratio decreases as the initial temperature of the limit mixture is increased, the ratio at the

FIG. 7.

Showing the oxygen/combustible ratio for the upper-limit mixtures of various gases and air at various temperatures, the ratio at the ordinary temperature being taken as unity.
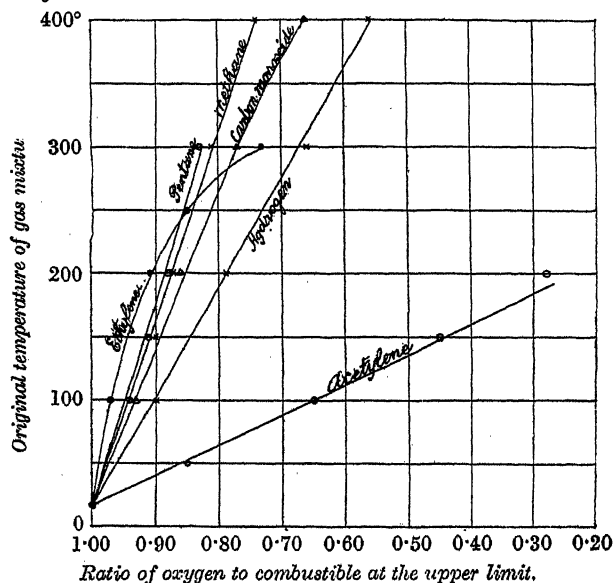
ordinary temperature being taken as unity.   The ratios determined seem to lie on approximately straight lines for all the gases examined except ethylene, in which case a small original fall rapidly increases as the temperature rises.   The decrease in ratio appears to be far more rapid for acetylene than for the other gases, whilst that for methane appears to be much the same as that for pentane.

The lower-limit results may also be examined from a slightly different angle.

The figures given in Table IV are taken from, or calculated from values given in, Tables I and II.   The new table shows the calorific values of the lower-limit mixtures both at the ordinary temperature

TABLE IV.

Showing the calorific values of certain lower-limit mixtures at the ordinary and at a much higher temperature, and certain relations between these and the heat needed to bring the lower-limit mixture up to its ignition temperature and to the temperature of the second limit experiment.

Gas used.	Calorific value of lower limit mixture at 17°±3°. C_1.	400°.* C_2.	C_1-C_2.	Heat in Cals. needed to brin mixtur from 17 to 400°.* C_3.	$100(C_1-C_2-C_3)/C_1$.	$\dfrac{100(R-1)}{R}$. See Table I.	Ignition temperature.
Hydrogen	536	359	177	261	−16	22	585°
Carbon monoxide	1108	775	333	261	+6	57	651
Methane	1197	912	285	270	+1	57	700
Ethylene	1087	788	299	265	+3	66	543
Acetylene	873	659	214	193	+2	67	429
Pentane	1193	951	242	199	+4	—	400 ?

* 300° was the temperature used in both these cases for acetylene and for pentane. The ignition temperature of pentane is given as 400°, but this is merely a rough estimate based on the values of Dixon and Coward for methane and for ethane (575°), and on that of Tizard and Pye for heptane (300°).

and at a chosen high temperature. The amount of heat needed to bring the lower-limit mixtures to these temperatures is also given, and it is easily seen that by subtracting this from the difference between the two former values we get the heat saved by determining the limit at the higher temperature. This is the portion of the heat unutilised for heating up the unburnt mixture at the ordinary temperature which is made use of at the higher temperature. If this higher temperature is considerably nearer the ignition temperature of the limit mixture than the ordinary temperature, the heat thus saved should form a fair proportion of the total heat lost at the ordinary temperature, as all losses should be cut down by the use of a higher initial temperature. The fifth column shows the heat saved at the higher temperature, whilst the sixth shows the total heat lost at the ordinary temperature, both being given as a percentage of the calorific value of the limit mixture at the ordinary temperature. In only one case—that of hydrogen—does the proportion of the total heat saved become significant. For hydrogen, not only has the heat saved a relatively greater value than in the other cases, but it is of a different sign, showing a considerably greater loss of heat at 400° than at the ordinary temperature. The ordinary ignition temperature theory thus seems to break down in this case. The same conclusion can

be drawn from the heat lost at various temperatures for the other gases, so that all the evidence obtained during the course of this work seems to show that the ordinary ignition temperature is not the effective ignition temperature during the propagation of flame.

Summary.

Limits for the propagation of flame downward have been determined in tubes 25 mm. in diameter and 1·5 metres long at various temperatures up to 400°, where possible, for mixtures of hydrogen, carbon monoxide, methane, ethylene, acetylene, and pentane with air. The results obtained agree reasonably well with some of the moderately recent results for the lower limits of methane in air, but do not accord with any of the upper-limit results in the literature. Incidentally, the latter do not agree amongst themselves.

The temperature–lower-limit curves obtained are very nearly straight lines, the limit figure falling by from 6 to about 8% per 100°. Similar curves for the upper limits are also straight lines in certain cases, but for ethylene and acetylene the upper-limit figures increase very rapidly at the higher temperatures.

Calculation showed that at the lower limit, for all the gases except hydrogen the theoretical flame temperature remained approximately the same throughout the whole temperature range. A consideration of these values and of the value of the limits at various temperatures is considered to support the view that the ignition temperature as ordinarily determined has little to do with the propagation of flame.

Determinations of upper limits for the propagation of flame in methane–air in 25 mm. and in 18 mm. tubes showed that the limits determined in the narrower tube increased less rapidly with temperature than did those determined in the wider tube. For the same gas mixture, much the same results were obtained for horizontal as for downward propagation.

XCVII.—*Styrylbenzopyrylium Salts. Part IV. γ-Styryl Derivatives of* 5 : 7-*Dihydroxy- and* 5 : 7-*Dimethoxy-2-phenyl-4-methylbenzopyrylium Chloride.*

By George Hugh Walker and Isidor Morris Heilbron.

It was shown in Part III (Buck and Heilbron, J., 1923, **123**, 2521) that in addition to α-styrylbenzopyrylium salts, γ-styryl derivatives could readily be prepared by the condensation of 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride with aromatic aldehydes. These salts differed from the α-class (J., 1922, **121**, 1198) in having a free hydroxyl group in position 7. In both series, the formation of quinonoid anhydro-bases was noted in all chlorides containing a *p*-hydroxyl group in the styryl residue, but whereas with 4'-hydroxy-2-styrylbenzopyrylium chloride (I) the change was brought about on dilution with water alone, this only occurred with 4' : 7-di-hydroxy-2-phenyl-4-styrylbenzopyrylium chloride (II) in presence of dilute sodium hydroxide or sodium carbonate solution.
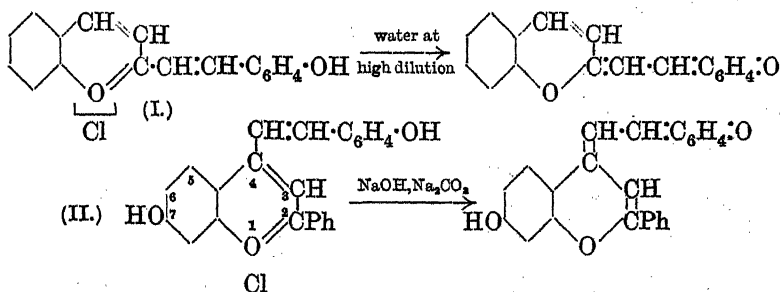
With the object of studying the effect of an additional hydroxyl group on the colour of the γ-styrylbenzopyrylium salts and their solutions and also of determining whether the non-formation of the blue quinonoid anhydro-base on water dilution was due to the presence of the free hydroxyl group in the 7-position, a series of 5 : 7-dihydroxy-γ-styrylbenzopyrylium chlorides has been prepared, and their properties compared with the analogously constituted 5 : 7-dimethoxy-γ-styrylbenzopyrylium salts. The general method of preparation was similar to that employed by Buck and Heilbron (*loc. cit.*). Phloroglucinol and its dimethyl ether were each con-densed with benzoylacetone as described in the experimental portion, and the resulting benzopyrylium chlorides then further condensed with aromatic aldehydes.

The 5 : 7-dihydroxy-γ-styrylbenzopyrylium chlorides are highly-coloured, crystalline salts which show the usual behaviour of members of this series in that they sinter and melt with decompos

tion. They are characterised by their sparing solubility in comparison with the corresponding members of the 7-hydroxy series (formula II).   The effect of the hydroxyl group in the 5-position is otherwise by no means pronounced, but there is an unexpected noticeable decrease in colour both of the dry salts and of their solutions in alcohol. As with the salts of the 7-hydroxy-γ-styryl series, a deep blue or bluish-violet colour is developed on addition of a few drops of dilute sodium hydroxide or sodium carbonate solution to the red, aqueous alcoholic solution of all chlorides containing a p-hydroxy-group in the styryl residue.   In the case of the p-methoxy-analogues, the red colour remains unimpaired, as quinonoid formation is impossible and isomerisation to the colourless carbinol bases does not occur in this series.

The 5 : 7-dimethoxy-2-phenyl-4-styrylbenzopyrylium chlorides closely resemble the corresponding hydroxy-salts, but their solutions in alcohol are considerably deeper in colour, indicative of the increased auxochromic influence of the methoxyl groups, and they are very much more soluble in alcohol and glacial acetic acid.   One of the most interesting compounds of this series is the green, crystalline 5 : 7 - dimethoxy - 4' - dimethylamino - 2 - phenyl - 4 - styrylbenzopyrylium chloride, which is the first salt to be isolated containing the $-NMe_2$ grouping in the free state in a form suitable for analysis.

Their chief point of interest lies in the fact that on dilution with water they behave similarly to the salts of the α-styryl series. Thus, whereas   4' : 5 : 7-trihydroxy - 2 - phenyl - 4 - styrylbenzopyrylium chloride (III) only passes into the quinonoid anhydro-base (IV) on addition of alkali, the same change takes place with 5 : 7-dimethoxy-4'-hydroxy-2-phenyl-4-styrylbenzopyrylium   chloride   on   dilution with water alone.
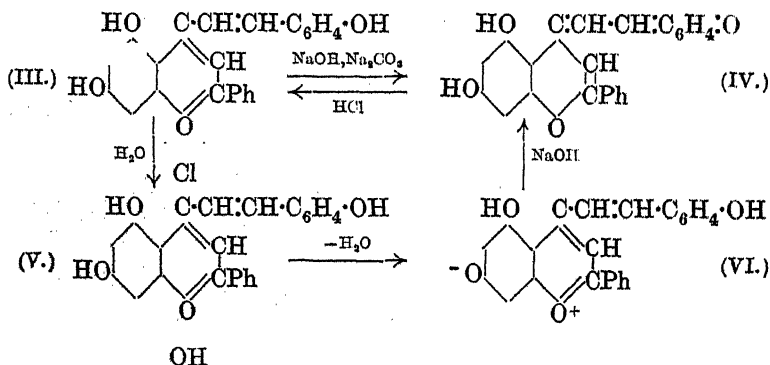
It would thus appear that the presence of the 7-hydroxyl group is undoubtedly the retarding influence in the rearrangement to

quinonoid anhydro-base. This may possibly be due to the colour base (V), which is doubtless formed on hydrolysis of III, passing, without change of colour, into the more stable betaine (VI), which is immediately transformed by alkali into the quinonoid base (IV).

<div align="center">EXPERIMENTAL.</div>

5 : 7-*Dihydroxy-2-phenyl-4-methylbenzopyrylium chloride*, orange-red needles, was prepared by a slight modification of Bülow and Wagner's method (*Ber.*, 1901, **34**, 1782), 80% formic acid being employed with advantage as solvent in place of glacial acetic acid. The double *ferrichloride* separates from glacial acetic acid in presence of dry hydrogen chloride in orange-yellow needles. It contains 1 molecule of water, half of which is lost after standing for two months in an exsiccator over concentrated sulphuric acid (Found : C = 41·7 ; H = 3·1 ; Fe = 12·2. $C_{16}H_{13}O_3Cl_4Fe,\frac{1}{2}H_2O$ requires C = 41·7 ; H = 3·0 ; Fe = 12·1%).

4' : 5 : 7-*Trihydroxy-2-phenyl-4-styrylbenzopyrylium Chloride* (III) —5 : 7-Dihydroxy-2-phenyl-4-methylbenzopyrylium chloride (10 g.) and *p*-hydroxybenzaldehyde (5 g.) were boiled under reflux for 2 hours with absolute alcohol (50 c.c.), a stream of dry hydrogen chloride being passed continually into the boiling solution. The resulting reddish-brown powder crystallises from pure formic acid, in which it is only slightly soluble, after saturation with dry hydrogen chloride, in dark brown needles with metallic reflex, m. p. 260° (Found : C = 70·8 ; H = 4·3. $C_{23}H_{17}O_4Cl$ requires C = 70·3 ; H = 4·3%).

5 : 7-*Dihydroxy-4'-methoxy-2-phenyl-4-styrylbenzopyrylium chloride*, prepared in a similar manner, separates, on standing in the ice-chest, as a reddish-brown powder. It crystallises best from a mixture of equal parts of glacial acetic acid and formic acid (80%) after saturation with hydrogen chloride, in bluish-red needles, which become crimson over solid sodium hydroxide in an exsiccator. In alcohol the solution is orange, showing an intense green fluorescence which is destroyed on addition of water. Alkali produces no change in colour (Found : C = 70·5 ; H = 4·5. $C_{24}H_{19}O_4Cl$ requires C = 70·8 ; H = 4·7%).

5 : 7-*Dihydroxy-4'-dimethylamino-2-phenyl - 4 - styrylbenzopyrylium Chloride*.—A solution containing the parent chloride (10 g.), *p*-dimethylaminobenzaldehyde (5 g.), and absolute alcohol (50 c.c.) was heated on the water-bath for 1 hour without hydrogen chloride being introduced, owing to the ready formation of the unstable yellow hydrochloride of the salt, which does not separate from solution. After leaving for 24 hours in an ice-chest, the bluish-green, amorphous powder was filtered off. It was only sparingly

soluble in alcohol (greenish-blue colour) and acetone (purple solution), but could not be obtained in crystalline form. The green alcoholic solution changes, on addition of dilute sodium hydroxide solution, into deep blue, excess of the reagent giving a brown, cloudy solution. The double *ferrichloride* separates on boiling the crude chloride (3 g.) with commercial ferric chloride (4 g.) in glacial acetic acid (30 c.c.). It crystallises from boiling acetone, in which it is readily soluble (purple solution), in dark green needles (m. p. 270°). If dry hydrogen chloride is passed into a solution of this iron salt in glacial acetic acid (cooled in ice), golden-yellow needles of the unstable hydrochloride are obtained (Found : C = 51·6; H = 4·1; Fe = 9·8. $C_{25}H_{22}O_3NCl_4Fe$ requires C = 51·5; H = 3·8; Fe = 9·6%).

The *perchlorate,* formed on addition of 20% perchloric acid to an alcoholic solution of the chloride, crystallises in dark green needles, whilst the *diperchlorate,* obtained by treating a suspension of the chloride in glacial acetic acid with 40% perchloric acid, is orange-yellow. These salts were too explosive to admit of analytical data being obtained.

5 : 7 - *Dimethoxy - 2 - phenyl - 4 - methylbenzopyrylium Chloride.*— Phloroglucinol dimethyl ether (10 g.), prepared according to Robinson's method (J., 1924, **125**, 193), and benzoylacetone (10·5 g.) were heated under reflux with ether (30 c.c.) until solution was complete. The warm solution was saturated with dry hydrogen chloride during 1 hour, refluxed for a further 10 minutes, and allowed to cool in a slow stream of dry hydrogen chloride. After 12 hours, the whole had solidified, and the crude salt was recrystallised from a small quantity of absolute alcohol previously saturated with hydrogen chloride gas, separating in yellow-brown needles, m. p. 180°, readily soluble in water or dilute hydrochloric acid [Found : C = 62·7; H = 5·3; Cl (Carius) = 15·7.

$$C_{18}H_{17}O_3Cl, \tfrac{1}{2}H_2O, \tfrac{1}{2}HCl$$

requires C = 62·8; H = 5·4; Cl = 15·5%). The *ferrichloride,* which separates from an alcoholic mixture of the reactants on saturation with hydrogen chloride gas, forms long, yellow needles from acetone, m. p. 215° (Found : C = 44·6; H = 3·8; Fe = 11·7. $C_{18}H_{17}O_3Cl_4Fe$ requires C = 45·1; H = 3·5; Fe = 11·7%).

5 : 7-*Dimethoxy-4'-hydroxy-2-phenyl-4-styrylbenzopyrylium Chloride.*—A suspension containing the parent chloride (3·2 g.) and p-hydroxybenzaldehyde (1·2 g.) in 18 c.c. of absolute alcohol was heated to boiling and saturated with dry hydrogen chloride during ½ hour. After 12 hours, the crude salt was filtered, washed with ether, and crystallised from a mixture of equal volumes of formic acid and glacial acetic acid containing hydrogen chloride. It separated

in glistening, blue-green needles, m. p. 230°, somewhat sparingly soluble in absolute alcohol to a deep red solution which changed to intense blue either on dilution with water or on addition of dilute alkali (Found : C = 71·5 ; H = 4·7. $C_{25}H_{21}O_4Cl$ requires C = 71·3 ; H = 5·0%).

The isomeric 5 : 7-*dimethoxy*-2'-*hydroxy*-2-*phenyl*-4-*styrylbenzopyrylium chloride*, prepared ïn a similar manner, separates from 80 % formic acid in brick-red needles (m. p. 110°) which in moist air tend to resinify. The colour of this salt is characteristic and, unlike the 4'-hydroxy salt, the red alcoholic solution does not change to blue on simple dilution with water, but only on addition of alkali. The blue colour, which is not so intense, gradually fades to light yellow (Found : C = 68·2 ; H = 5·4. $C_{25}H_{21}O_4Cl,H_2O$ requires C = 68·4 ; H = 5·2%).

3' : 5 : 7-*Trimethoxy*-4'-*hydroxy* - 2 - *phenyl* - 4 - *styrylbenzopyrylium Chloride*.—This salt separates as a crystalline sludge on treating the parent chloride (3 g.) in absolute alcohol (18 c.c.) with vanillin (11·5 g.) and rapidly saturating the solution with dry hydrogen chloride. It crystallises from 80% formic acid in brownish-black needles with metallic reflex (m. p. 210°). The red alcoholic solution changes to deep blue on dilution with water alone (Found : C = 68·8 ; H = 5·0. $C_{28}H_{23}O_5Cl$ requires C = 69·2 ; H = 5·1%).

5 : 7-*Dimethoxy*-4'-*dimethylamino*-2-*phenyl* - 4 - *styrylbenzopyrylium chloride* is prepared by gently refluxing an alcoholic solution of 5 : 7-dimethoxy-2-phenyl-4-methylbenzopyrylium chloride and *p*-dimethylaminobenzaldehyde on the water-bath for 15 minutes in absence of hydrogen chloride. A deep blue solution is obtained from which the salt gradually crystallises out during 2 days; it forms glistening, bright green needles from absolute alcohol (m. p. 190°). The alcoholic solution, which is peacock green, changes to deep blue on addition of dilute alkali. On addition of concentrated hydrochloric acid the alcoholic solution becomes orange, due to formation of the styrylbenzopyrylium chloride hydrochloride. Concentrated alkali precipitates a colourless, gelatinous mass which probably consists of the pseudo-base (Found : C = 69·8 ; H = 6·2. $C_{27}H_{26}O_3NCl,H_2O$ requires C = 69·6 ; H = 6·0%). The *ferrichloride* separates from acetone in small, green crystals soluble in glacial acetic acid, alcohol, or acetone with a deep purple colour (Found : C = 53·2 ; H = 4·5 ; Fe = 9·2. $C_{27}H_{26}O_3NCl_4Fe$ requires C = 53·1 ; H = 4·3 ; Fe = 9·2%).

XCVIII.—*Styrylbenzopyrylium Salts. Part V. Distyryl Derivatives of 7-Hydroxy-2 : 4-dimethylbenzopyrylium Chloride.*

By Isidor Morris Heilbron, George Hugh Walker, and Johannes Sybrandt Buck.

The styrylbenzopyrylium chlorides hitherto prepared (J., 1922, **121**, 1198; 1923, **123**, 1395, 2521; and preceding paper) have contained only one styryl residue either in the α- or γ-position to the pyrylium oxygen atom. The present communication deals with the preparation of distyrylbenzopyrylium salts containing styryl residues in both the α- and the γ-position, the parent chloride being 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride, $OH \cdot C_6H_3 < {}^{CMe \vdots \gamma H}_{OCl \vdots CMe}$.

If an aldehyde, A, is condensed with this chloride, and the mono-styrylbenzopyrylium derivative obtained further condensed with another aldehyde, B, the resulting distyryl chloride will be different from the one obtained by condensation in the reverse order, provided the aldehyde B in the second case unites with the same methyl group as the aldehyde A in the first case. The comparison of various distyryl chlorides has shown that, in the majority of cases, the pairs of distyryl chlorides containing the same two aldehydes, condensed in the reverse order, have different physical and chemical properties. From this it follows that, although both methyl groups are highly reactive, one must act preferentially in the formation of the monostyryl chloride, which will consequently be a pure compound and not a mixture of α- and γ-derivatives, provided equimolecular quantities of aldehyde and pyrylium chloride are allowed to interact. On the other hand, when two molecules of aldehyde are employed per molecule of the parent chloride, distyrylbenzopyrylium chlorides are formed. In the condensation of anisaldehyde with 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride, two isomeric styrylbenzo-pyrylium chlorides, a violet and a blue salt, have been isolated by slightly varying the conditions of the reaction. As these give rise to different distyryl derivatives, it is obvious that they represent the α- and γ-monostyryl compounds. Unfortunately, it has proved impossible to fix definitely the configuration of any of these chlorides, and for the purpose of describing them it has been determined to assign to the majority the α-configuration.* That this is in all probability correct may be adduced by collateral evidence drawn

* Borsche and Wunder (*Annalen*, 1916, **411**, 64) assign analogous configurations to the monostyryl chlorides obtained on condensation of the parent chloride with salicylaldehyde, piperonal, and resorcylaldehyde.

from other sources. Thus, in the quinoline series, it has repeatedly been found that the methyl group is more reactive in quinaldine than in lepidine, and Bogert and Nabenhauer have recently shown that the methyl group in 2-methylquinazoline condenses more rapidly with phthalic anhydride than the corresponding group in the 4-position (*J. Amer. Chem. Soc.*, 1924, 46, 1932). The only apparent exceptions among the compounds studied are the blue monoanisyl chloride (I) and the monovanillin chloride, to which the γ-configuration has been assigned. The reason for this is that the former yields with *p*-hydroxybenzaldehyde a distyrylbenzopyrylium chloride (IV) identical with the one isolated by condensing 4′ : 7-dihydroxy-2-styryl-4-methylbenzopyrylium chloride (III) with anisaldehyde, and different from that obtained by condensing the isomeric violet anisyl chloride (II) with *p*-hydroxybenzaldehyde.
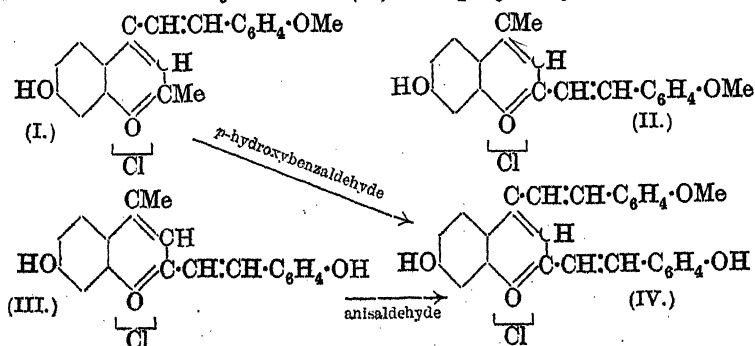
Similarly, the monovanillin chloride (V) gives with piperonal a distyryl chloride (VII) identical with the salt obtained by condensation of 7-hydroxy-3′ : 4′-methylenedioxy-2-styryl-4-methylbenzopyrylium chloride (VI) with vanillin.
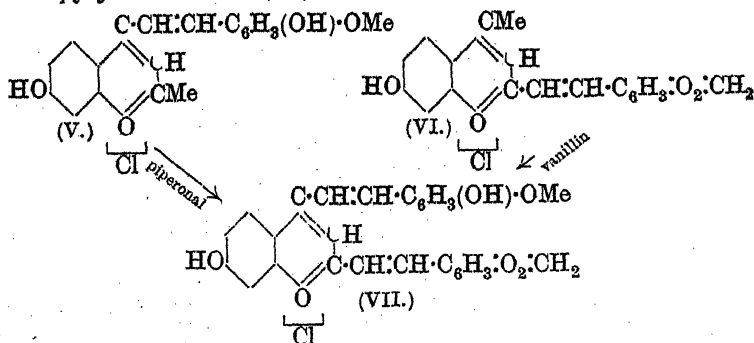
That the vanillin derivative is abnormal, differing in constitution from the other monostyrylbenzopyrylium salts, is supported by the

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fact that it is the only brown monostyryl chloride found in this series.

It is thus clear that these two monostyryl salts are certainly differently constituted from the majority and, on the assumption that the latter are α-derivatives, they must accordingly be represent-atives of the γ-monostyryl series.

In their properties, both the mono- and the di-styrylbenzo-pyrylium chlorides closely resemble the salts formerly described. A characteristic feature is the deep green colour of almost all the chlorides containing a p-hydroxy-group in the styryl residue. This distinguishes them from the analogous chlorides of the previous series (p. 685), which are usually brown or red with bluish-green reflex. The monostyryl salts dissolve in alcohol with an orange or a red coloration. The distyryl chlorides, on the other hand, form intense reddish-purple solutions in this solvent. All members of this series containing a p-hydroxyl group in either styryl residue show the characteristic change of colour from red to blue on addition of dilute alkali to an alcoholic solution of the chloride, but in no case could this colour change be brought about by dilution with water alone.

EXPERIMENTAL.

7-*Hydroxy*-2 : 4-*dimethylbenzopyrylium chloride* was prepared from resorcinol and acetylacetone by von Bülow's method (*Ber.*, 1901, **34**, 1189). In order to obtain consistent results in condensations, it was found necessary to purify the crude salt by dissolving it in the minimum quantity of 80% formic acid, and reprecipitate by addition of a mixture of ether and ethyl acetate. Under these conditions it usually forms a bulky, pale yellow product, but if still dark in colour, the above treatment must be repeated.

4′ : 7-*Dihydroxy*-2-*styryl*-4-*methylbenzopyrylium Chloride* * (Formula III).—7-Hydroxy-2 : 4-dimethylbenzopyrylium chloride (7·7 g.) was gently boiled with formic acid (20 c.c. of 80%) until a deep emerald-green colour was produced, allowed to cool to 40°, and mixed with p-hydroxybenzaldehyde (4·1 g.), the whole being rapidly saturated with dry hydrogen chloride. After 2 days, the solid was filtered and recrystallised from 90% formic acid saturated with hydrogen chloride, forming glistening, beetle-green crystals, m. p. 260°. If the formic acid contains more than 20% of water,

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* Owing to the fact that experimental proof regarding the position of the styryl residue is lacking, the possibility of the alternative configuration as 4′ : 7-dihydroxy-4-styryl-2-methylbenzopyrylium chloride, although less prob-able on theoretical grounds, cannot be ignored. This applies equally to all other monostyryl and unsymmetrical distyryl salts described in this com-munication.

the chloride separates in yellowish-green crystals. It is readily soluble in formic acid and glacial acetic acid, sparingly soluble in absolute alcohol with an intense red colour which is changed to deep blue on addition of dilute sodium hydroxide solution [Found : after 1 month over solid KOH, C = 63·5; H = 4·9; Cl (Carius) = 10·1. $C_{18}H_{15}O_3Cl,HCO_2H$ requires C = 63·2; H = 4·7; Cl = 10·0%].

7-*Hydroxy*-4'-*methoxy*-2-*styryl*-4-*methylbenzopyrylium chloride* (formula II) was similarly prepared. The crude product crystallises from 80% formic acid (deep orange-red solution) in small, purple prisms, m. p. 160°. The orange-red solution in absolute alcohol (N/1000 dilution) shows a brown fluorescence, which is immediately destroyed on addition of water.

If, in the preparation of the above chloride, the anisaldehyde is added to the boiling solution, the isomeric salt (formula I) is formed, which crystallises from 80% formic acid in blue-black needles, m. p. 150°. The colours in solution are identical with those of the purple form. As these two varieties lead to different distyrylpyrylium chlorides, it is evident that they are structurally different [Found : (purple form) C = 66·2; H = 5·5; Cl = 10·1. (Blue form) C = 66·1; H = 5·4. $C_{19}H_{17}O_3Cl,H_2O$ requires C = 65·8; H = 5·5; Cl = 10·2%].

4' : 7-*Dihydroxy*-3'-*methoxy*-4-*styryl*-2-*methylbenzopyrylium chloride* (formula V) crystallises from glacial acetic acid containing 10% of absolute formic acid in small, brown crystals, sparingly soluble in alcohol to a carmine-red solution which becomes blue in presence of dilute alkali (Found : C = 60·8; H = 4·9; Cl = 9·2. $C_{19}H_{17}O_4Cl,H_2CO_2$ requires C = 61·4; H = 4·9; Cl = 9·1%).

3' : 4' : 7-*Trihydroxy*-2-*styryl*-4-*methylbenzopyrylium chloride* is prepared by the direct condensation of protocatechualdehyde with the parent chloride under precisely the same conditions. It separates from the reaction mixture over-night and is recrystallised from absolute formic acid saturated with hydrogen chloride, in which solvent it dissolves with a deep red colour. Green needles having a brilliant golden reflex, only sparingly soluble in glacial acetic acid and in absolute alcohol, the solution in the latter solvent being carmine and changing to deep Prussian blue on addition of alkali (Found : C = 65·1; H = 4·9; Cl = 10·5. $C_{18}H_{15}O_4Cl$ requires C = 65·3; H = 4·5; Cl = 10·7%).

7-*Hydroxy*-4'-*dimethylamino*-2-*styryl*-4-*methylbenzopyrylium Chloride.*—A solution containing 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride (7 g.) and *p*-dimethylaminobenzaldehyde (5 g.) in absolute alcohol (25 c.c.) was refluxed on a water-bath for 1 hour. Towards the end of the reaction a bronze-violet, crystalline powder was rapidly deposited from the deep blue solution and, after stand-

ing over-night, was filtered. It is only very sparingly soluble in alcohol or glacial acetic acid to a deep blue solution and in formic acid to an olive-green. Owing to its remarkable insolubility, it could not be recrystallised and it was accordingly purified by repeated washing with small quantities of absolute alcohol. Addition of concentrated hydrochloric acid to an alcoholic solution of the chloride gives rise to a yellow solution containing the dichloride (Found : C = 66·5; H = 6·1; Cl = 9·7. $C_{20}H_{20}O_2NCl,H_2O$ requires C = 66·7; H = 6·1; Cl = 9·8%).

4′ : 4″ : 7 - *Trihydroxy* - 2 : 4 - *distyrylbenzopyrylium* *Chloride*.*— 7-Hydroxy-2 : 4-dimethylbenzopyrylium chloride (7·7 g.) and *p*-hydroxybenzaldehyde (8·2 g.) are suspended in hot absolute alcohol (25 c.c.) and a rapid stream of dry hydrogen chloride is passed in during ½ hour, when an intense ruby-red solution is formed. This is set aside and heated occasionally during 5 days, by which time a brilliant, bronze-green powder will have separated. Recrystallised from a mixture of absolute formic acid containing 15% of glacial acetic acid, the salt forms dark green crystals, m. p. 240°, only sparingly soluble in alcohol and acetic acid with reddish-purple coloration. The alcoholic solution changes to Prussian blue on addition of alkali (Found : C = 68·7; H = 5·2; Cl = 7·8. $C_{25}H_{19}O_4Cl,H_2O$ requires C = 68·7; H = 4·8; Cl = 8·1%).

7-*Hydroxy*-4′ : 4″-*dimethoxy*-2 : 4-*distyrylbenzopyrylium chloride* is best prepared by saturating a solution (15 c.c. of alcohol) of the purple monoanisyl chloride (8·2 g.) and anisaldehyde (3·4 g.) with dry hydrogen chloride at room temperature and then refluxing for about an hour. After 12 hours, the blue-green crystalline mass is filtered and kept over cold glacial acetic acid to remove traces of anisaldehyde, which prevent its separation on recrystallisation. It forms greenish-blue prisms from boiling glacial acetic acid, m. p. 170°, and is sparingly soluble in absolute alcohol to a carmine solution with faint brown fluorescence. Addition of alkali changes the colour first to green and then to pale yellow (Found : C = 69·8; H = 5·3; Cl = 7·5. $C_{27}H_{23}O_4Cl,H_2O$ requires C = 69·7; H = 5·4; Cl = 7·6%).

* The positions of the various groups in the distyryl series are numbered as follows :
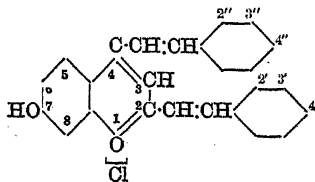
7-Hydroxy-4'-methoxy-4''- dimethylamino - 2 : 4 - distyrylbenzopyrylium chloride was prepared by boiling a solution in alcohol (40 c.c.) of the purple monoanisyl salt (10·9 g.) with *p*-dimethyl-aminobenzaldehyde (4·9 g.) under reflux for ½ hour without the use of hydrogen chloride. The solution rapidly assumed a deep blue colour and, after 12 hours, the separated black powder was filtered, washed with ether, and recrystallised from glacial acetic acid, forming small, black crystals, m. p. 200°, soluble in alcohol to a deep blue solution which changed to purple on addition of a few drops of dilute alkali. In concentrated hydrochloric acid the colour is orange (Found : C = 67·4; H = 5·9; Cl = 7·6. $C_{28}H_{26}O_3NCl,2H_2O$ requires C = 67·8; H = 6·1; Cl = 7·2%).

4' : 7-Dihydroxy-4''-methoxy-2 : 4-distyrylbenzopyrylium Chloride (Formula IV).—4' : 7-Dihydroxy-2-styryl-4-methylbenzopyrylium chloride (13 g.) and anisaldehyde (8·0 g.) were refluxed with absolute alcohol (20 c.c.), saturated with dry hydrogen chloride, for 1½ hours. The somewhat oily mass was washed with alcohol and recrystallised from 80% formic acid saturated with hydrogen chloride, forming dark-brown, shining needles, m. p. 220°, sparingly soluble in glacial acetic acid or alcohol. The solution in the latter solvent is reddish-purple, which changes to deep blue on addition of alkali (Found : C = 68·9; H = 5·2; Cl = 7·9. $C_{26}H_{21}O_4Cl,H_2O$ requires C = 69·2; H = 5·1; Cl = 7·9%).

This chloride is identical with the salt obtained by the condensation of blue monoanisyl chloride (I) with *p*-hydroxybenz-aldehyde under precisely similar conditions.

The isomeric 4'' : 7-dihydroxy-4'-methoxy-2 : 4-distyrylbenzo-pyrylium chloride prepared from the violet monoanisyl chloride and *p*-hydroxybenzaldehyde crystallises from 80% formic acid in dark green crystals, m. p. 160°. The colour in alcohol is identical with that of its isomeride, but on addition of alkali only a dark-green colour is produced, which, however, develops a blue tinge on dilution with water (Found : C = 66·3; H = 5·3. $C_{26}H_{21}O_4Cl,2H_2O$ requires C = 66·5; H = 5·3%).

3' : 4' : 7-Trihydroxy-4''-methoxy-2 : 4-distyrylbenzopyrylium chloride separates from 80% formic acid in emerald-green needles, m. p. 240°, sparingly soluble in alcohol with deep reddish-purple colour (Found : C = 64·6; H = 4·9. $C_{26}H_{21}O_5Cl,2H_2O$ requires C = 64·4; H = 5·2; Cl = 7·3%).

The isomeric *3'' : 4'' : 7-trihydroxy-4'-methoxy-2 : 4-distyryl-benzopyrylium chloride* obtained by the condensation of the violet monoanisyl chloride (II) with protocatechualdehyde forms a dark-green, crystalline powder, m. p. 210°, also containing 2 mols. of H_2O (Found : C = 64·7; H = 5·2; Cl = 7·5 %).

3' : 4' : 7-*Trihydroxy* - 3'' : 4'' - *methylenedioxy* - 2 : 4 - *distyrylbenzo-pyrylium   Chloride.*—3' : 4' : 7-Trihydroxy-2-styryl-4-methylbenzo-pyrylium chloride (8·2 g.) and piperonal (3·7 g.) in absolute alcohol (15 c.c.) were saturated with dry hydrogen chloride and refluxed for 2 hours. After 12 hours, the separated salt was filtered and recrystallised from 90% formic acid saturated with hydrogen chloride. It forms emerald-green needles with faint golden reflex, m. p. 255°, and is sparingly soluble in glacial acetic acid or alcohol to a deep reddish-purple solution, the colour of the latter becoming pure blue on dilution with water (Found : $C = 62·9$; $H = 4·7$. $C_{26}H_{19}O_6Cl,2H_2O$ requires $C = 62·6$; $H = 4·6$; $Cl = 7·1\%$).

The isomeric 3'' : 4'' : 7-*trihydroxy*-3' : 4'-*methylenedioxy*-2 : 4-*distyrylbenzopyrylium chloride*, similarly obtained from 7-hydroxy-3' : 4'-methylenedioxy-2-styryl-4-methylbenzopyrylium chloride and protocatechualdehyde, forms a dark green, crystalline powder, m. p. 200° (Found : $C = 62·2$; $H = 4·7$; $Cl = 7·2\%$).

4'' : 7-*Dihydroxy*-3''-*methoxy*-3' : 4'-*methylenedioxy* - 2 : 4 - *distyryl-benzopyrylium chloride* (formula VII) was prepared by the condensation of 7-hydroxy-3' : 4'-methylenedioxy-2-styryl-4-methylbenzo-pyrylium chloride (8·5 g.) with vanillin (3·8 g.). The salt crystallises from 80% formic acid as a dark green, crystalline powder, m. p. 180°, and is identical with the salt obtained by condensation of the monostyryl vanillin chloride (V) with piperonal (Found : $C = 62·9$; $H = 5·0$; $Cl = 6·9$. $C_{27}H_{21}O_6Cl,2H_2O$ requires $C = 63·2$; $H = 4·9$; $Cl = 6·9\%$).

THE UNIVERSITY, LIVERPOOL.   [*Received, January 14th, 1925.*]

XCIX.—*A Redetermination of the Atomic Weight of Boron.*

By HENRY VINCENT AIRD BRISCOE and PERCY LUCOCK ROBINSON.

In 1921, when the work here described was undertaken, the atomic weight of boron, usually taken as 11·0, was evidently uncertain to the extent of one or two units in the first decimal place. Consideration of all the available data for this atomic weight (Briscoe, Robinson, and Stephenson, this vol., p. 150) shows that the values published before 1922 range from $B = 11·529$ to $B = 10·703$ and

give in mean approximately B = 10·95.   Actually the uncertainty in this mean was even greater than appears from the figures, as it has been shown (*loc. cit.*) that there is reason to regard with grave suspicion all those determinations (14 out of a total of 24) dependent on the weighing of fused borax.

Therefore, in planning this investigation, we resolved to make a preliminary series of analyses to establish the method and then to carry out side by side three distinct and independent series of determinations, using samples of boron from widely separated, known sources, subjecting each sample before analysis to a rigorous purification, and ensuring particularly that all the samples had comparable treatment.

This method of attack was prompted also by another motive : the desire to inquire experimentally whether for boron the isotope-ratio is always and everywhere the same.   Hitherto, in the great majority of atomic weight determinations, attention has been wholly concentrated on attaining great purity of the substance taken for analysis and the *origin* of that material has not been considered.   Yet in the one case, that of lead, where materials of different known origin have been thoroughly investigated, results of the greatest interest and importance have accrued.   These investigations, of course, arose from, and served to confirm, speculations as to the radio-active origin of lead, but it seems possible that an equally exhaustive examination of specimens of some of the lighter elements from different sources might throw some light upon the problem, at present quite obscure, of the origin and history of the elements in general.   Several atomic weight determinations for elements other than boron, referred to in more detail later and published during the progress of this research, have evidently been undertaken with this possibility in view : but it seems desirable to state it clearly here as a primary reason for our work.

The choice of a ratio for measurement was made only after a careful review of all the known compounds of boron.   Excluding borax, for the reason already given, there remain few compounds at all likely to be obtainable pure and of constant and definite composition.   Among these boron trisulphide and the additive compound of boron trifluoride and ammonia seem promising, but they have been little investigated and involve methods of analysis either difficult and untried or obviously unsuited to precise work. Boron trichloride and tribromide are definite and stable compounds, the properties of which are well-known : although extremely sensitive to moisture, they appear to be the compounds best suited to

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precise analysis. Therefore it was decided to determine in this
case the ratio $BCl_3 : 3Ag$.

Preliminary tests made by adding to a litre of pure water 1·5 g.
of boric acid and 2·5 g. of silver nitrate gave a perfectly clear
solution whether nitric acid (12·0 c.c. of concentrated acid) were
added or not, and thus showed that silver borate is not precipitated
under the conditions obtaining in the titration of a chloride with
silver in presence of nitric acid by the usual procedure. Therefore
the method of analysis adopted consisted in weighing boron
trichloride in sealed glass bulbs, breaking the bulbs in water, and
titrating the hydrochloric acid in the resulting dilute solution of
boric and hydrochloric acids with silver nitrate prepared from a
weighed amount of pure silver, the end-point being ascertained
nephelometrically.

Weighing.

Throughout this work the special Oertling balance with the
separately enclosed steel beam and the set of weights described in a
previous communication (Robinson and Briscoe, this vol., p. 138)
were used. The balance was kept in a darkened room having a
north aspect and was illuminated by artificial light falling normally
on the front of the balance. Both the zero and the sensitivity,
the latter set at about 33 scale divisions per milligram, remained
very constant throughout. As the inequality of the arms was
very small and constant for all loads and as relative weights only
were desired, all weighings and calibrations were made directly and
not by reversal or substitution.

In weighing out metallic silver, etched buttons of nearly the
desired weight, with pieces of pure silver wire and foil as make up,
were weighed out (a valuable check) on a standard No. 7 S. W.
Oertling balance, dried for 12 hours at 250° in an electrically heated
glass oven, cooled beside the balance in a desiccator over solid
caustic potash, transferred to the balance pan, and weighed within
½ hour. Vacuum weights of silver were ascertained by applying
to the apparent weight a correction determined by the density of
silver (10·49) and the density of air at the pressure and temperature
observed during weighing.

The weights of boron trichloride were ascertained in the manner
previously described in detail with illustrative data (Briscoe and
Little, J., 1914, 105, 1330; Briscoe, J., 1915, 107, 72). Bulbs
and stems filled with dry air were each weighed on three separate
occasions against a tare, the temperature and barometric pressure
being noted at the time of each weighing. After being filled and
sealed off from the stem, bulbs and stems were again weighed on
two separate occasions against the same tare. Then the external

volume of each bulb was determined by weighing in air and in water and, the density (as the mean of concordant determinations on four samples) and actual weight of the glass of the bulb being known, the internal volume of the bulb, and hence the weight of air originally contained in the bulb was calculated. The relative vacuum weight of the boron trichloride in the bulb is evidently the apparent weight (increase in excess weight over tare) *plus* this weight of air. Before each weighing the bulbs and stems and tares were carefully wiped with well-washed pure linen and then allowed to stand in the balance case for 8—12 hours.

This method of weighing sensitive materials is evidently less well known than it should be. Weatherill (*J. Amer. Chem. Soc.*, 1924, 46, 2442) has recently confirmed that its error is probably no greater than the error of weighing, 0·01—0·02 mg., but is apparently unaware of the prior description and use of the method by one of us, as the procedure in experiment and calculation is again described in detail and no reference is made to the prior publication.

The weights and gold half-milligram rider were repeatedly calibrated to ascertain their relative weights in air, and were always used on the same (right hand) balance pan : in all weighings, a correction was applied for the calibration error.

The error in weighing was less than 0·02 mg. and weights of boron trichloride are stated to the nearest 0·01 mg. Weights of silver are stated in the same manner, but are affected by the possible error in the nephelometric determination of the end-point, approximately 0·00005 g.

It has been stated (Manley, *Phil. Trans.*, 1913, 212, [A], 227) that objects dried in an enclosed space alongside solid caustic potash can become contaminated with alkali. As this drying agent was extensively used in this and earlier determinations, the experiments described below were made to ascertain whether such contamination occurs under the conditions of the normal use of this drying agent.

As a test for alkali a solution of phenolphthalein, made very faintly pink with alkali, was used : one drop of it added to 0·05 c.c. of N/100-caustic soda (0·00002 g.) in 10 c.c. of water gave a distinct red coloration.

1. During more than 2 years the upper and lower compartments of the balance case had been dried by means of vessels containing caustic potash stood close against the back of the case and renewed from time to time, as the alkali deliquesced. Therefore the back pane of glass was removed from the case, flooded with about 5 c.c. of water, and the washings were tested with phenolphthalein. No trace of alkali could be detected.

2. A fairly rapid current of air saturated with water vapour was passed first through a 50% solution of caustic potash, secondly through a tower packed with solid caustic potash, and then on to the surface of about 10 c.c. of phenolphthalein solution placed in a clean wash-bottle, which had been used for distilled water for 5 years. This experiment was run continuously for 500 hours, but no trace of red coloration developed.

Therefore it is clear that caustic potash does not contaminate an air stream passed over it or glass surfaces in its neighbourhood.

Purification of Reagents.

The methods adopted for the purification of all the accessory reagents and of the main supply of silver have been sufficiently described (Robinson and Briscoe, loc. cit.). It is here only necessary to add that the small pieces of silver used to adjust the weights of the silver buttons were in part pieces of wire of various gauges remaining from a previous investigation (Briscoe, loc. cit.) and in part pieces cut from thin sheet silver with clean steel scissors, etched with nitric acid, well washed, and dried at 250°. The sheet silver was prepared by hammering and then rolling a large button of pure silver between sheets of parchment.

Three samples of silver were used, namely, Silver I, Silver A, and Silver B. The preparation of the materials A and B has been previously described (Robinson and Briscoe, loc. cit.). Silver I, used only in the preliminary work, was metal prepared from silver nitrate by the Stas bisulphite method and subsequently dissolved in nitric acid and reprecipitated in the same way. There is every reason to believe that the samples of silver were uniform and that A and B were closely similar : results obtained with them should, therefore, be strictly comparable. Any constant impurity in the silver would, of course, affect the absolute value of the results, but numerous investigations have shown that the method employed for preparing the silver yields a product containing but 1 part of impurity in 300,000 parts, the effect of which on the results is negligible in comparison with that of other sources of error.

Preparation and Purification of Boron Trichloride.

Sources.—The boron trichloride used in the preliminary series of analyses (sample i) was prepared from boric acid of unknown origin in stock in the laboratory. That used for the three main series was prepared from the following materials :

Sample (ii) Crude boric acid from the neighbourhood of Volterra, Tuscany.

Sample (iii) Boracite from Sultan Tchair, Asia Minor.

Sample (iv) Colemanite (calcined) from Death Valley, California, U.S.A.

We are indebted to Messrs. Borax Consolidated, Ltd., for supplies of these minerals and for detailed information as to their origin, and would here express our thanks to Mr. R. C. Baker, managing director of that company, for his personal interest in securing for us this essential starting material.

Preparation of Boric Acid.—Sample (i) was used without purification : sample (ii) was recrystallised once from a filtered solution in dilute hydrochloric acid. The boracite ($6MgO,MgCl_2,8B_2O_3$) sample (iii) and colemanite ($Ca_2B_6O_{11},xH_2O$) sample (iv) were each dissolved in boiling 1 : 1 hydrochloric acid, and the solution was diluted with its own bulk of boiling water, filtered at the boiling point in a jacketed funnel, and cooled to obtain a crop of white, crystalline boric acid, which was filtered off and dried.

Preparation of Boron Trichloride.—Dumas's method (*Ann. Chim. Phys.*, 1826, [ii], **31**, 436) was tried by heating in chlorine (a) a mixture of ground boric oxide glass and carbon, and (b) charcoal soaked in hot concentrated boric acid solution, and dried; and also by striking an arc between a carbon rod and mixture (a) in an atmosphere of chlorine. The heating of boron nitride in chlorine and of boric oxide glass in carbon tetrachloride vapour were also investigated, but none of these methods gave a yield of boron trichloride sufficient to warrant its adoption. The heating of boric acid with phosphorus pentachloride (Gustavson, *Ber.*, 1870, **3**, 426; 1871, **4**, 975) seemed so likely to introduce volatile phosphorus chlorides as an impurity that it was not attempted. Thus it became necessary to adopt the wasteful and troublesome process of preparing and chlorinating elementary boron.

Anhydrous boric oxide was obtained by gradually feeding boric acid into a clay crucible kept at a bright red heat until the crucible was three-quarters filled, and keeping the melt at 1000°, until all evolution of steam had ceased. The resulting glass was poured on to a cold iron plate, crushed, and then ground in a Weatherhead crusher to pass a sieve of 50 meshes to the linear inch.

This oxide was then reduced with magnesium, according to the method usually attributed to Moissan, although it had been used by earlier workers (Phipson, *Proc. Roy. Soc.*, 1864, **13**, 217 ; Jones, J., 1879, **34**, 42; Winkler, *Ber.*, 1890, **23**, 772 : see also Moissan, *Compt. rend.*, 1892, **114**, 319; Weintraub, *Trans. Amer. Electrochem. Soc.*, 1909, **16**, 165; Ray, J., 1914, **105**, 2162). A mixture of 70 parts of powdered boric anhydride with 50 parts of magnesium powder contained in a clay crucible and covered with a 2-inch layer of powdered charcoal was heated in a furnace until reaction

took place. Then the air supply to the furnace was immediately cut off and the crucible and its contents were allowed to cool in a reducing atmosphere. This procedure served greatly to minimise the serious loss of boron by reoxidation, found to occur when the porous mass produced by the reaction was exposed to air whilst hot. Working details of the successful method are given, as failure attended attempts to conduct the reaction in closed vessels in an atmosphere of hydrogen and by other methods. The furnace used in all this work, a 20 lb. "Captive Fire" furnace, fired with a correct mixture of coal-gas and air, both supplied under pressure, proved specially convenient for the operations described. The coke-like product, freed from admixed lumps of charcoal, was powdered, digested for 24 hours with concentrated hydrochloric acid to decompose borides and dissolve metallic oxides present, and boiled with an equal bulk of water. After settling, the clear liquor was decanted, the residue was again twice extracted with boiling dilute hydrochloric acid and was then filtered off, washed, and dried at 100°. Some difficulty was encountered in converting this boron to the trichloride. At first, it was heated in a current of chlorine in a silica tube wound with nichrome wire and heated electrically, but it was soon found that, even at a dull red heat, the boron trichloride rapidly attacked the silica, one tube being perforated in a few hours, and the product contained considerable quantities of silicon tetrachloride. An attempt to protect the silica from attack by flooding the inner surface with concentrated magnesium nitrate solution and igniting this to oxide, thus brasquing the tube with magnesia, proved useless. An alundum tube was even more seriously attacked and was speedily blocked up by volatilised aluminium chloride : it also proved so porous as to permit a serious amount of chlorine to leak into the atmosphere : hence its use was abandoned. Ultimately, it was found that a tube of hard Jena glass, heated at about 450—500° only, by slipping over it a wider silica tube heated electrically, was scarcely attacked, could be washed out and re-used repeatedly, and gave a product almost free from silicon chloride.

Gas from a cylinder of liquid chlorine passed through a pressure gauge and safety valve consisting of a T-tube dipping into a tall jar of concentrated sulphuric acid, and then through a Drechsel bottle containing the same acid, into the reaction tube. This tube, about 36 inches long and ¾ inch in diameter, was fitted at one end with a waxed cork carrying the leading tube for chlorine : at the other end a glass adapter, attached by wide rubber tubing, led the products into a glass receiving vessel, of the form shown in Fig. 3 (R_1, R_2, etc.), cooled with solid carbon dioxide. This refrigerant

was used because it was found that ordinary freezing mixtures allowed some chlorine (b. p. —33°) to pass and this carried away a considerable proportion of the boron trichloride (b. p. +12·5°). At the end of each run both tubes of the receiver were drawn down to capillaries (to permit reopening) and sealed before the blowpipe.

Another serious trouble in the earlier chlorinations was the frequent stoppage of the tubes with a white solid, which proved to be boric anhydride. Though, as others have noted (see, *e.g.*, Stock and Holle, *Ber.*, 1908, **41**, 2095), the boron was undoubtedly impure, the proportion of oxide it contained was quite insufficient to account for the quantity found in the tubes. Therefore it seemed probable that the trouble must be due to water persistently retained by the boron powder, and it was found that if this boron, immediately before chlorination, was dried by heating to redness in a silica tube in a current of dry hydrogen, the deposition of boric anhydride was so far minimised as to make the process workable : this procedure was therefore adopted throughout the preparations of boron trichloride.

Purification of Boron Trichloride.—The crude material contained considerable amounts of chlorine, hydrogen chloride, boric oxide, ferric chloride, and insoluble matters, and owing to the thoroughly unsatisfactory nature of the method of preparation many other impurities may have been present, including such volatile chlorides as chloroform, carbon tetrachloride, phosphorus trichloride, silicon tetrachloride, etc. Therefore, it was necessary to adopt a very elaborate process of purification, and as, evidently, the value of the determination wholly depends on the efficiency of this process, it must be described in detail.

The purification of sample (i) for the preliminary series was, of course, experimental and its actual treatment is sufficiently shown in Fig. 1. All the main series samples (ii), (iii), and (iv) received substantially identical treatment comprising the following stages :

1. Distillation from various receivers into a large bulb.

2. Distillation into the single-column fractionating still.

3. Distillation in this still, with thorough fractionation, whereby chlorine and hydrogen chloride were almost completely removed.

4. Standing and frequent shaking in a sealed bulb with mercury for 3 months or longer.

5. Systematic fractional distillation in three stages, conducted in dry air at about atmospheric pressure in the " three-column still."

6. Standing and frequent shaking in a sealed bulb with sodium amalgam for about 3 months.

7. Fractional distillation into five fractions in a vacuum.

8. Fractional distillation of the middle fraction in a vacuum, and collection in bulbs.

9. In the case of samples (iii) and (iv) a middle fraction, collected among the bulbs for analysis, was further redistilled, leaving a residual fraction, and the distillate transferred to weighed bulbs by pouring.

This typical scheme of purification for the main samples is shown diagrammatically in Fig. 1. With regard to the treatment of individual samples it is only necessary to remark that the treatment

FIG. 1.
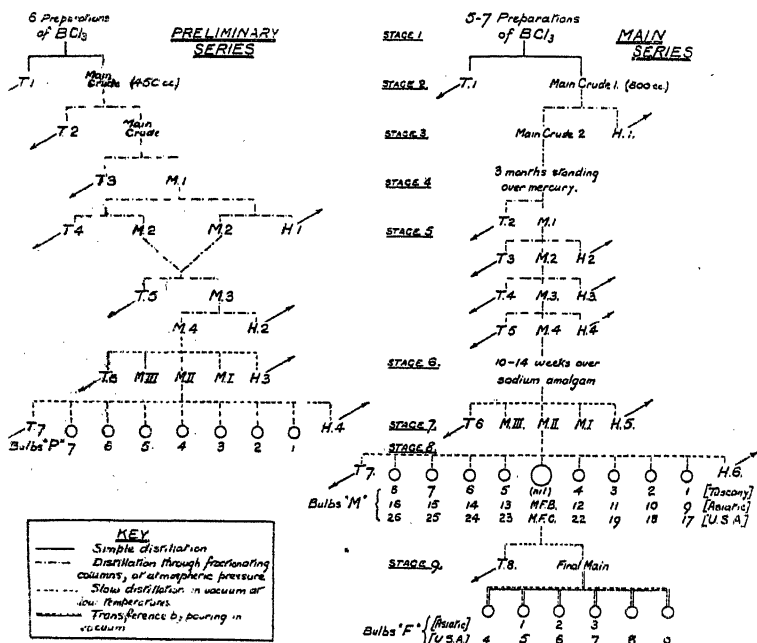
of sample (ii) differed from that of (iii) and (iv) in the following details : (a) stage 5 comprised two separate handlings in a " two-column still " instead of one in the "three-column still " described below : (b) After the sample had been sealed up at the end of stage 5, it was found that the sodium amalgam had been omitted from the bulb. Fortunately, as the bulb had a "special joint," this could be rectified by transferring the contents to another similar bulb containing sodium amalgam : an attempt to effect this by distillation failed owing to the receiver becoming air-locked, but by freezing the amalgam solid in the bottom of the receiver with liquid air, it became possible to invert the apparatus and

transfer the boron trichloride by pouring, and this was successfully accomplished; (c) the quantity of material in the final main fraction of stage 6 was little more than sufficient to fill eight bulbs and yielded a middle fraction (marked "nil," Fig. 1) too small to carry to stage 9.

The apparatus employed may be understood by reference to the "one-column" and "three-column" stills used for stages 3 and 5

FIG. 2.
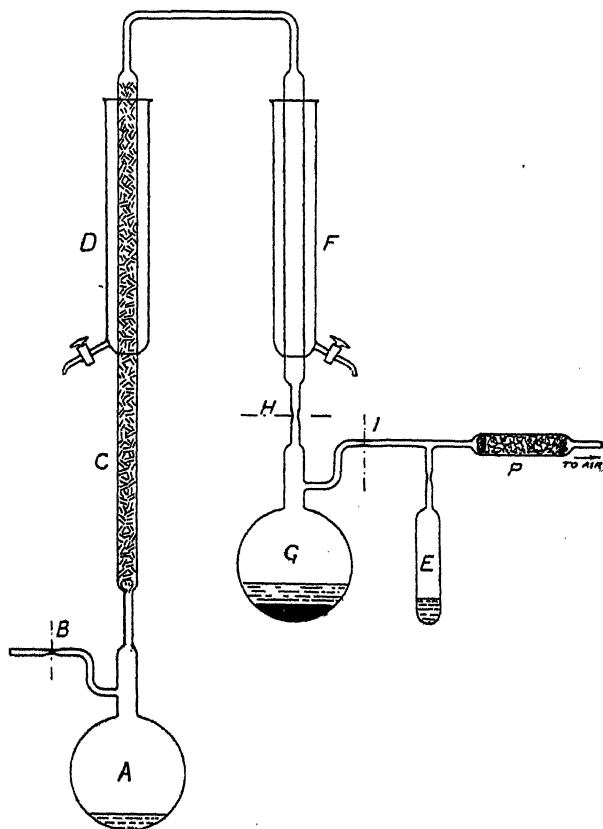
of the main series purification (Fig. 1) shown in Figs. 2 and 3. The columns C were 2 cm. in diameter and 60 cm. in packed length, filled with hollow cylindrical glass beads 4 mm. in diameter and 4 mm. long (Raschig, Eng. Pat. 1914, No. 6288), supported by a perforated bulb at the bottom. The upper half of each was surrounded by a glass jacket containing water kept at 10° by stirring in crushed ice, and acted as a regulated temperature still-head.

That such columns are very efficient (see, *e.g.*, Lessing, *J. Soc. Chem. Ind.*, 1920, **40**, 115T) was confirmed by the fact that, during the first distillation, a sharp demarcation between the deep yellow chlorine and colourless boron trichloride occurred within 2 cm. in the column and moved steadily up as the last of the chlorine was removed.

In using the " one-column still " (Fig. 2), the apparatus was filled with dry air, and then crude boron trichloride, previously collected into one vessel by distillation from the several receivers, was distilled into A *via* the side-tube, B, and this was then sealed off at the constriction. The jacket, D, having been cooled to 10°, A was immersed in water at 15—20° until the chlorine had been distilled off and swept out of the apparatus. Then, F and G being kept warm enough to prevent any condensation, a considerable head fraction was distilled into E and sealed off. Finally, F was cooled with ice and G with solid carbon dioxide, and a main fraction was distilled into G, which was then sealed off at H and I, leaving a considerable tail fraction in A. During the distillation the apparatus was open to the atmosphere through an efficient phosphorus pentoxide tube, P. In G, the boron trichloride stood, and was frequently shaken, during about 3 months in contact with pure mercury previously placed in the bulb.

The " three-column still," shown diagrammatically in Fig. 3, consisted of four bulbs, S, of 800 c.c. capacity, the first three each having a column, C, leading to a receiver, R, open to air through a phosphorus pentoxide guard tube, P, and connected *via* a mercury valve, V, to the next bulb. The whole apparatus was clamped around a single large retort-stand and sealed together. From Fig. 3a, showing the construction of the valves, it is evident how, by lowering or raising the mercury level in the U-tube, connexion between the two sides of the valve may be made or broken, and thus how it is possible to direct vapour into any desired part of the apparatus and conduct a systematic fractional distillation without bringing the boron trichloride into contact with any material other than dry glass, mercury, and air.

The valves V having been sealed with mercury, the apparatus was first dried by passing in at J a current of dry air and allowing it to pass away first through P_1, and then successively through P_2, P_3, and P_4, the capillary exit tubes being sealed or cut open as required. During this operation all parts of the apparatus in turn were repeatedly heated to 150—200°. Then a quantity of pure sodium amalgam was filtered into S_4 through the tube K, and this tube was sealed off. The current of dry air was now reversed, passing in at P_4 and out at J, and the bulb, G, containing mercury

and a main fraction of crude boron trichloride from the previous distillation, was connected at J by a glass-and-rubber joint flexible enough to allow the sealed capillary of G to be broken within it. Then M 1 was cooled, the lower part in ice and the neck by a collar of solid carbon dioxide, and G was warmed at 15° until the liquid had distilled over, leaving a small tail fraction in G, which was finally sealed off at L.

The material was now completely protected against moisture, and the distillations constituting stage 5 (Fig. 1) were carried out in a manner which is obvious from Fig. 3 and the preceding description.

FIG. 3.
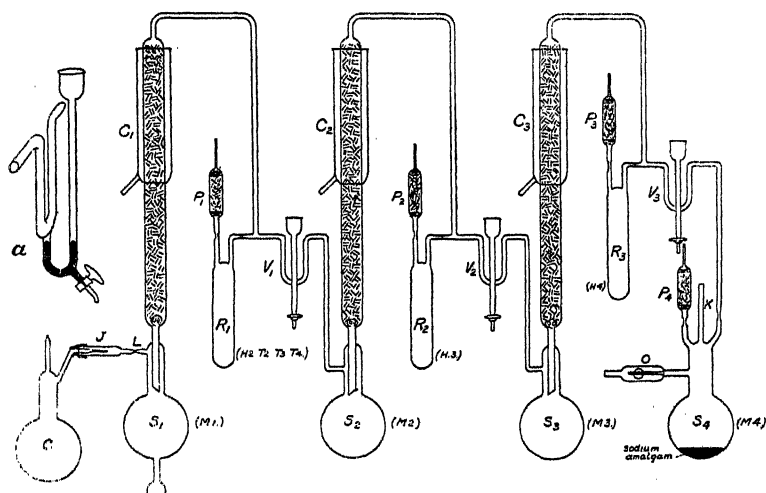
Rejected head and tail fractions were collected in the bulbs R, which were sealed off, immediately they had received the fractions shown (in brackets) against them, in the order R_2, R_3, R_1. The final main fraction, M 4, was collected and sealed up with the sodium amalgam in bulb S_4, provided with a " special joint," O : it stood in the bulb, and was frequently shaken, during 10—14 weeks.

During the last distillation of this stage readings of a thermometer enclosed in the upper part of column C_3 gave readings for the boiling point of boron trichloride which, when corrected for the observed atmospheric pressure at the time of distillation, agreed closely with the value 12·5° found by Stock and Priess (Ber., 1914, 47, 3109).

The remaining stages of the purification and the transference into bulbs were carried out in a vacuum by a method essentially

similar to that first described by one of us (Briscoe and Little,
loc. cit.), and since used in several other precise investigations (see,
e.g., Brauner and Krepelka, *J. Amer. Chem. Soc.*, 1920, 42, 1917;
Krepelka, *ibid.*, p. 925; Baxter, Weatherill, and Holmes, *ibid.*,
p. 1194; Baxter, Weatherill, and Scripture, *Proc. Amer. Acad.
Arts Sci.*, 1923, 58, 245).

The " special joint " which makes this method possible was used
by one of us in the purification of vanadyl trichloride early in 1912,
and was described as new in 1914, but it has recently come to our
knowledge that the use of a closely similar device, though for
another purpose, was described (Bruner and Bekier, *Z. Elektrochem.*,
1912, 18, 369) prior to our publication.

One small, but important, improvement was made by inter-
posing between the special joint, S, and the bulbs, B (Fig. 4), a

FIG. 4.
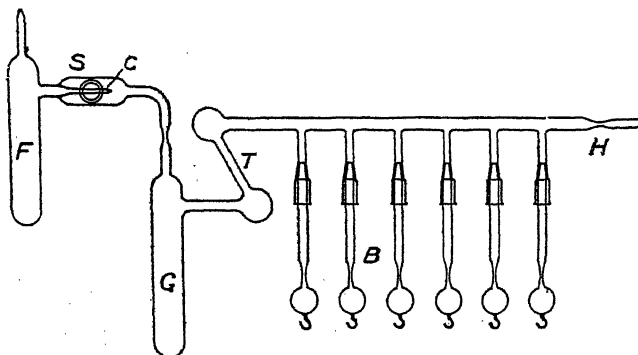
two-bulb trap of the form shown at T, designed to prevent any
fragments of broken glass being carried over into the bulbs by the
stream of vapour when the capillary C is broken. Weatherill (*loc.
cit.*) also has found this precaution desirable.

In two cases the quantity of boron trichloride in the main frac-
tion was more than enough to fill eight bulbs, and the excess was
collected as a middle fraction in a separate bulb, F (Fig. 4), and
subsequently transferred to weighed bulbs in the following way.

The bulb F was fused on to the remainder of the system shown
in Fig. 4 and then was heated, repeatedly evacuated, and finally
sealed off at H. The special joint K was then opened, and the
liquid was distilled into G, leaving a last fraction in F, which was
then sealed off. The whole apparatus was next inverted and the
liquid transferred to the bulbs by pouring, assisted by alternate
heating and cooling of the bulbs, in alcohol at − 20° and in liquid
air respectively.

This operation was performed with the material for the Final Series B and C : in both cases the tail fraction in F was carefully distilled into the side tube and left no trace of visible residue.

Tests of the Efficiency of the Method of Purification.

This is evidently a case in which the efficiency of the scheme of purification is exceptionally important and every attempt was made to secure direct experimental evidence on this point. The effect of the possible impurities upon the atomic weight is shown in Table I, whence it is evident that the elimination of boric oxide, chlorine, and hydrogen chloride is specially important.

TABLE I.

Impurity.	Change in the atomic weight of boron produced by the presence of 0·1% of the impurity in BCl_3.	B. p.
Boron trioxide, B_2O_3	+0·108	—
Chlorine, Cl_2	−0·012	−33·6°
Hydrogen chloride, HCl	−0·008	−83·1
Silicon tetrachloride, $SiCl_4$	+0·009	+59·6
Phosphorus trichloride, PCl_3	+0·017	+76
Arsenic trichloride, $AsCl_3$	+0·042	+130·2
Antimony trichloride, $SbCl_3$	+0·046	+223·5

By a fortunate chance, at a later stage of the purification of the material for the Preliminary Series, a phenomenon was observed which has, apparently, escaped the notice of other workers using boron trichloride. From mere curiosity, the residual fractions from some of the less pure samples of boron trichloride were distilled to dryness : they left a colourless, non-crystalline, and apparently gelatinous or syrupy residue which, when warmed to 40—50°, intumesced and left a white, amorphous solid. On standing in boron trichloride vapour, the solid first became translucent and then deliquesced to a liquid : it was evidently volatile with boron trichloride and probably consisted wholly or largely of boric acid or boric oxide. It was investigated by the following experiments, making use of fractions from the distillations of the Preliminary Series, transferred in a vacuum by means of special joints in the usual way.

A quantity of pure boron trichloride, leaving on evaporation practically no trace of residue, was distilled (a) partly on to powdered boric oxide glass, dried at 300° in a vacuum, and (b) partly on to boric acid dried at 100° in a vacuum. In both cases the solid dissolved and the solution yielded a distillate that left on evaporation a large, gummy residue, showing precisely the behaviour described above. Thus it was proved that boric acid and boric oxide are volatile in boron trichloride.

In order to ascertain whether this residue could be separated by distillation, a bulb, A, containing about 30 g. of boron trichloride (T 6 of the Preliminary Series) was connected by its special joint to a second evacuated bulb, B. When the liquid was distilled into B, a small but distinct residue was left in A : when the distillate in B was completely redistilled back into A, a much smaller, but still distinctly visible patch of residue remained in B. Then about one-quarter of the liquid in A was repeatedly distilled into B and *poured* back into A until no trace of residue remained on warming B. Finally, about two-thirds of the liquid was distilled into B and then redistilled back into A, when but a very small trace of residue remained in B. These observations prove that the residue can be progressively diminished by fractional distillation in a vacuum, and render it probable that it can thus be eliminated.

It is well established that mercury reacts with anhydrous chlorine : hence the prolonged treatment given in this case (until a clean surface of the metal remained bright indefinitely) should have ensured the removal of all free halogen. There exists no such evidence that anhydrous hydrogen chloride reacts with sodium amalgam, therefore a sealed bulb containing about 100 g. of clean 2% sodium amalgam and a sealed thin capillary tube containing about 0·15 g. of water were placed in a stout cylindrical bulb sealed to a closed-end mercury pressure gauge, and about 40 g. of good boron trichloride were distilled into and sealed up in the bulb. The bulb and capillary containing the amalgam and water were broken by vigorous shaking and the apparatus was set up in a room having a fairly constant temperature and kept under observation for several weeks.

There was a steady evolution of gas and rise of pressure, and this continued at a diminishing rate for more than 14 days, affording clear evidence that hydrogen chloride does react with sodium amalgam under the anhydrous conditions obtaining in the process of purification.

A separate experiment showed that pure boron trichloride had no action on sodium amalgam.

The removal of impurities was also followed analytically : about 6 c.c. of boron trichloride were decomposed with water, the solution was divided into equal parts, and these were treated (*a*) with nitric acid and (*b*) with nitric acid and ammonium molybdate, warmed, and allowed to stand several days. Several of the earlier tail fractions gave (*a*) a distinct gelatinous precipitate, probably silica, and (*b*) a slight yellow precipitate of ammonium phosphomolybdate : the later tail fractions gave no evidence whatever of silica or phosphoric acid.

Method of Analysis.

In previous determinations of the ratio of boron trichloride to silver, the bulbs have usually been broken in dilute pure ammonia. The presence of excess of ammonia, obviously desirable as a precaution against loss of hydrogen chloride if the solution has to be filtered from the fragments of the bulb, was clearly unnecessary in this case, as all the weighings requisite to determine the vacuum weight of boron trichloride had been made before the analysis was begun.

In each titration the bulb containing boron trichloride, suspended by its hook from a hooked glass rod, was washed and then lowered into about 2000 c.c. of pure water contained in a thoroughly clean resistance glass bottle of 4000—6000 c.c. capacity. The bottle was closed with its carefully fitted and polished stopper, cooled in ice for an hour to reduce the internal pressure, and then vigorously shaken to break the bulb. The reaction between boron trichloride and water was quickly over and produced a perfectly clear and colourless solution, but left some fog in the bottle : therefore the bottle was well shaken at frequent intervals until the fog had completely disappeared and then allowed to stand for at least 3 hours before it was opened.

Meanwhile a quantity of pure silver, calculated to be within a few tenths of a milligram of that required, having been accurately weighed, was dissolved in pure aqueous nitric acid (1 : 1) in a Jena glass solution flask of the special form previously described (Briscoe, J., 1915, **107**, 78), and the solution was heated to boiling, to expel nitrous fumes, cooled, and diluted to about 1200 c.c.

The stopper was carefully removed from the titration bottle and rinsed, the fragments of the glass bulb, especially the capillary ends, were broken up by means of a long, stout glass rod, and the silver solution and rinsings were transferred to the bottle *via* the side tube in the manner described in detail elsewhere.

This transference and all subsequent operations were carried out in orange light in a darkened laboratory set aside solely for these titrations and kept free from all possible sources of contamination with chlorine or silver.

The solution was gently swirled during the addition of silver and immediately thereafter the bottle was stoppered, vigorously shaken at frequent intervals during 2—3 hours, allowed to stand at room temperature for 7—10 days, being well shaken twice or thrice each day, and then packed in ice for about 48 hours.

Then 100 c.c. of the clear supernatant liquid were withdrawn with a pipette and used for duplicate nephelometric tests in the

TABLE II.
Data and Results of Analyses.

Number of analysis.	Sample of silver.	Relative vacuum wt. (g.) of BCl₃.	Relative vacuum wt. (g.) of silver.	Ratio : BCl₃/3Ag.	Atomic wt. of boron (Ag = 107·880; Cl = 35·457).	Individual and average deviations from mean.
			Preliminary Series.			
P 1	Silver 1	7·10616	19·61748	0·362236	10·854	+0·002
P 2						
P 3	,, 1	8·06893	22·28012	0·362158	10·829	−0·023
P 4	,, 1	9·91393	27·37313	0·362177	10·835	−0·017
P 5						
P 6	,, 1	7·42801	20·49990	0·362344	10·889	+0·037
				Means	10·852	±0·020
			Main Series.			
		A. Boron from Boric Acid, Volterra, Tuscany.				
M 1						
M 2	Silver A	7·73567	21·35379	0·362262	10·862	+0·022
M 3	,, B	9·83151	27·14230	0·362221	10·849	+0·009
M 4	,, A	7·88427	21·76764	0·362201	10·843	+0·003
M 5	,, A	6·61346	18·26253	0·362133	10·821	−0·019
M 6						
M 7	,, A	7·51389	20·74865	0·362139	10·823	−0·017
M 8				Means	10·840	±0·014
		B. Boron from Boracite, Sultan Tchair, Asia Minor.				
M 9						
M 10	Silver A	7·88217	21·76472	0·362153	10·827	+0·008
M 11	,, B	7·00794	19·35154	0·362139	10·823	+0·004
M 12	,, A	11·56846	31·94600	0·362126	10·818	−0·001
M.F.B.						
M 13	,, A	12·04670	33·26752	0·362116	10·815	−0·004
M 14	,, B	11·39071	31·45640	0·362111	10·814	−0·005
M 15	,, A	8·45278	23·34215	0·362125	10·818	−0·001
M 16				Means	10·819	±0·004
		C. Boron from Colemanite, Death Valley, California, U.S.A.				
M 17						
M 18	Silver A	9·93543	27·42992	0·362212	10·846	−0·009
M 19*	,, B	6·69247	18·47861	0·362174	10·834	−0·021
M 22	,, A	6·87297	18·97723	0·362169	10·832	−0·023
M.F.C.						
M 23	,, A	8·66792	23·92939	0·362229	10·852	−0·003
M 24	,, B	8·08918	22·32812	0·362287	10·870	+0·015
M 25	,, A	5·95008	16·42010	0·362366	10·896	+0·041
M 26				Means	10·855	±0·019
		Final Series B (from fraction M.F.B., Main Series B).				
F 1	Silver B	5·96256	16·46538	0·362127	10·819	+0·001
F 2	,, B	5·83978	16·12666	0·362120	10·816	−0·002
F 3	,, B	5·31851	14·68670	0·362131	10·820	+0·002
				Means	10·818	±0·002
		Final Series C (from fraction M:F.C., Main Series C).				
F 4	Silver B	2·94096	8·11982	0·362195	10·841	+0·001
F 5	,, A	4·86840	13·44182	0·362184	10·837	−0·003
F 6	,, A	4·89699	13·52005	0·362202	10·843	+0·003
F 7	,, A	5·72597	15·80980	0·362179	10·836	−0·004
F 8	,, A	9·24458	25·52406	0·362190	10·839	−0·001
F 9	,, B	4·69097·	12·95092	0·362211	10·846	+0·006
				Means	10·840	±0·003

* Bulbs M 20 and M 21 were tares.

usual manner (Briscoe and Little, *J.*, 1914, **105**, 1322).   After an appropriate addition of silver or chloride had been made, in the form of a solution containing 0·0002 g. of silver or its equivalent per c.c., the bottle was again stoppered, shaken, and repacked in ice for 48 hours before another nephelometric test was made. When two such tests separated by 6—7 days agreed in showing that the equivalent concentrations of silver and chloride in the solutions differed by less than 2%, the titration was regarded as finished.

Statement and Discussion of Results.

Table II states the data and results for the Preliminary Series, the three Main Series, and the two Final Series.   In order to examine their significance, it is important to understand the relationship of the fractions with which they were obtained; therefore the names of the fractions not analysed are included in each group, the fractions are given in order of separation, *i.e.*, in the Preliminary and the Main Series the most volatile fractions first in each group, and the results are summarised in Table III.

TABLE III.

Summary of Results.

α = *Number of Fraction ;* β = *Atomic Weight of Boron (deduced).*

Main Series A.

α	M 1.	M 2.	M 3.	M 4.	M.F.A. ("nil")	M 5.	M 6.	M 7.	M 8.
β	·—	10·862	10·849	10·843	—	10·821	—	10·823	

Main Series B.

α	M 9.	M 10.	M 11.	M 12.	M.F.B.	M 13.	M 14.	M 15.	M 16.
β	—	10·827	10·823	10·818	—	10·815	10·814	10·818	

Main Series C.

α	M 17.	M 18.	M 19.	M 22.	M.F.C.	M 23.	M 24.	M 25.	M 26.
β	—	10·846	10·834	10·832	—	10·852	10·870	10·897	

Final Series B.

α	F 1.	F 2.	F 3.
β	10·819	10·816	10·820

Final Series C.

α	F 4.	F 5.	F 6.	F 7.	F 8.	F 9.
β	10·841	10·837	10·843	10·836	10·839	10·846

The analysis of fraction M 6 was lost through an accident, but with this exception every analysis begun was completed and is recorded in the table.   Both in the final transference to bulbs and in the analyses, the Series were dealt with in the order in which they are there named : the order of the analyses within each series was irregular and is immaterial.

The Preliminary Series, made with boron trichloride of unknown origin, was carried out simply to gain experience, and the variation

in the results was at first supposed to have no significance, especially
as the series contained but six bulbs and the *end* fractions were
analysed. As the results for the Main Series A, B, and C accumul-
ated, it was apparent that they exhibited a variation of similar
type and it at once became important to ascertain whether this
variation was accidental and due to errors in the analyses, or arose
from a real change in the composition of the boron trichloride on
distillation. By a fortunate accident, the quantity of boron
trichloride in the final main fraction of the vacuum distillations of
Series B and C had been much more than sufficient to fill eight bulbs,
and the excess in each case had been collected as a *middle* fraction
(M.F.B. and M.F.C.) in a large bulb provided with a special joint.
Therefore it was determined to transfer these fractions to weighed
bulbs by pouring in the manner described on p. 708, whereby,
evidently, the fraction as a whole was subjected to an efficient
separation from any less volatile impurity and yet any effect of
distillation in causing a variation in the composition of the con-
tents of individual bulbs was minimised. The effect of this is
apparent in the average deviation from the mean in Final Series B
and C, as contrasted with the corresponding figures for the Main
Series A, B, and especially C. Evidently the nature and extent
of the variations in the Final Series indicate that none of the
analyses is likely to give an atomic weight in error by more than
0·005 and that most of the results are probably within 0·002 or
0·003 of the truth.

This being so, it follows that certain systematic variations
apparent in the figures are *real* and require explanation. Three
types of systematic variation may be distinguished in discussion :

(1) The last results in each series are high and in one case show
a progressive increase.

(2) The first few values in each series diminish progressively to
a minimum.

(3) The results in both the Main and the Final Series C are
consistently higher than those in Series A and B.

Attention may first be directed to the possible impurities and
their effect as illustrated by the data in Table I. The table is not
exhaustive, as the possible impurities less volatile than boron
trichloride clearly include higher chlorides of silicon, arsenic,
phosphorus, etc., and also such compounds as chloroform and
carbon tetrachloride, which, being non-hydrolysable under the
conditions of analysis, would probably act, like boric oxide, as
inert diluents. It is immediately evident that all impurities *less
volatile* than boron trichloride tend to *increase* the apparent atomic
weight, whilst chlorine and hydrogen chloride, both *more volatile*

than boron trichloride, tend to *diminish* the apparent atomic weight.

The negative results of tests for silicon and phosphorus in the later tail fractions obtained in the course of purification would seem to ensure that the final main fractions could not have contained any less volatile chloride in an amount sufficient to have any perceptible effect on the atomic weight. There is not the same conclusive evidence that boric oxide was eliminated: visible traces of the gummy residue (although so small as to appear unweighable) were seen at late stages of the purification, and it seems reasonable to suppose that the increase at the ends of the series may be due to traces of boric oxide concentrated in the later fractions. This view accounts satisfactorily for the abnormally high values at the end of Main Series C, as this was much the *longest* series (the middle fraction M.F.C. being large) and the final bulbs in this case contained a considerably smaller fraction of the whole than did the corresponding bulbs in the other series.

The progressive decrease in the earlier values in the series cannot, apparently, be attributed to the presence of impurities. The concentration of volatile impurities would be greatest in the head fractions and would progressively diminish : their presence tends to lower the atomic weight, and therefore would cause a progressive *rise* in the value obtained with successive fractions. This consideration and the apparent efficacy of the chemical means used to eliminate chlorine and hydrogen chloride indicate that another explanation of this drift must be sought.

It is, we believe, to be found in the hypothesis that an isotopic separation has occurred. During the distillation into bulbs, in order to keep the pressure in the apparatus well below atmospheric pressure, the main bulk of boron trichloride was kept at or near the freezing point and the bulbs were cooled in liquid air. Under these conditions, the distillation must have been largely irreversible and, therefore, likely to effect such a separation.

Neglecting the doubtful isotope of chlorine, Cl^{39}, the elements concerned have each two isotopes and may conceivably form the eight compounds formulated below with their molecular weights and the percentage of chlorine they contain.

Compound.		Mol. wt.		% Cl.	
$B^{10} Cl_3^{35}$		115		91·4	
	$B^{11} Cl_3^{35}$		116		90·6
$B^{10} Cl_2^{35} Cl^{37}$		117		91·5	
	$B^{11} Cl_2^{35} Cl^{37}$		118		90·7
$B^{10} Cl^{35} Cl_2^{37}$		119		91·6	
	$B^{11} Cl^{35} Cl_2^{37}$		120		90·8
$B^{10} Cl_3^{37}$		121		91·7	
	$B^{11} Cl_3^{37}$		122		91·0

The lighter members of this group of compounds contain, for a given isotope of boron, a smaller percentage of chlorine than the corresponding heavier members : an increased weight percentage of chlorine causes an apparent diminution of the atomic weight : therefore a preponderance of the lighter compounds in the earlier fractions would account for the observed effect.

It should be remarked that separation in this order is determined by the difference in weight between the isotopes of chlorine. If the phenomenon under discussion is real and is due to a separation of compounds of isotopes, this order of separation affords definite evidence that in the great majority of molecules of these compounds the chlorine atoms are uniquely and permanently attached to their respective boron atoms. For if this were not so and, as is conceivable, chlorine atoms could migrate freely from one molecule of boron trichloride to another, then it is clear that for any group of B^{10} and B^{11} atoms, the chlorine in combination with either the lighter or the heavier boron atoms would, at any instant, have the same statistical average atomic weight, so that any separation by irreversible distillation would be determined solely by the relative weight of the boron atoms and would yield a series of fractions in which the atomic weight of boron would progressively increase.

This conclusion is in agreement with the work of von Hevesy and Zechmeister (Ber., 1920, 53, [B], 410), who have found that certain organic lead compounds in non-ionising solvents are not rendered radioactive by admixture with active lead chloride and hence conclude that no interchange of lead atoms can occur in the molecules of these compounds.

The difference in the final mean results for the three series merits more detailed consideration. The Preliminary Series and Main Series A' exhibit a comparatively large variation : if the foregoing hypothesis be true, this may have been caused by a specially slow and cautious distillation of the boron trichloride in these cases, and it would follow that the values about the middle of the series should be nearest the truth. Because M 2 yielded a high value and M 6 was lost, some uncertainty attaches to any deduction from Main Series A : having regard to the effect of the middle fraction M.F.A., we are of opinion that it indicates an atomic weight about 10·825 for the Tuscany boron. Excluding the value for M 2, the mean is 10·834 with a probable error ± 0·005.

Much more definite conclusions may be drawn with regard to Series B and C. Main Series B is very consistent, the result, 10·819, probable error ± 0·0014, is scarcely changed (to 10·818, p. e. ± 0·0013) if the result M 10 is rejected.

After another distillation, the middle fraction yielded the three results of Final Series B, giving the mean value 10·818, p. e. ± 0·0008. Combining these results, we obtain the value B = 10·8183.

Main Series C is less concordant, but the explanation above suggested for the high values of M 25 and M 26 seems to justify their exclusion : the mean for the remaining four determinations is 10·841, p. e. ± 0·003 : the mean including M 25 and M 26 is 10·855, p. e. ± 0·003. In this case the middle fraction, M.F.C., was much larger and gave the six concordant values of Final Series C, giving in mean 10·840, p. e. ± 0·002. Combining these results, we obtain substantially the same result, 10·8403 or 10·8407 respectively, whether the results of M 25 and M 26 are rejected or retained.

While this investigation was in progress, two other determinations of the atomic weight of boron have been published. Baxter and Scott (*Science*, 1921, **54**, 524) have stated that preliminary results obtained by the measurement of the ratios $BCl_3 : 3Ag$ and $BBr_3 : 3Ag$ indicated an atomic weight 10·83 ± 0·01. Their results have not been published in detail and cannot, therefore, be discussed in relation to our own : it is possibly significant that their result, probably obtained with boron of American origin, is comparatively high.

Hönigschmid and Birckenbach (*Ber.*, 1923, **56**, [*B*], 1467) determined the ratios $BCl_3 : 3Ag$ and $BCl_3 : 3AgCl$, using three samples of boron trichloride purified by fractional distillation in a vacuum by Stock and Kuss (*ibid.*, p. 1463). Unfortunately, the origin of their samples was, apparently, unknown. Sample I was derived from 40 c.c. of boron trichloride prepared (from boron and chlorine) and used by Stock, sometime prior to 1914, for the determination of certain physical constants (Stock and Priess, *Ber.*, 1914, **47**, 3109). Sample II was redistilled from 30 c.c. of crude material, newly made by the same method. Sample III was obtained from 50 c.c. of commercial boron trichloride. With these materials Hönigschmid and Birckenbach found the values (I) B = 10·840, (II) B = 10·818, (III) B = 10·825, which compare in striking fashion with the three results now recorded.

In calculating their final mean result, B = 10·820, they reject entirely the result B = 10·840, alleging that sample I had stood 4 months in the bulbs previous to analysis, and might have acted on the glass. In the course of our work we have repeatedly had clear evidence that no such action occurs, and our analyses, being spread, in the case of any given series, over several months, afford many clear proofs that such standing in sealed bulbs has no appre-

ciable effect on the apparent atomic weight. Moreover, it is difficult to see how, even if some corrosion of the glass occurred, it should affect the results.

Sample I should have been the purest of the three, since it was prepared from refined material, while samples II and III were prepared from crude material by a precisely similar process. Moreover, the data obtained with Sample I are, as a series, as consistent and apparently trustworthy as those for the other samples. The rejection of the result 10·840 deduced from Series I cannot, therefore, be justified unless solely on the ground of its discordance with the other results.

Thus it appears that, though they were made with much smaller quantities of material and that, perhaps, less rigorously purified than our own, the analyses of Hönigschmid and Birckenbach confirm our finding that different samples of boron may give values for the atomic weight differing by an amount much greater than any conceivable error of the determinations. We are informed by Messrs. Borax Consolidated Ltd. that, " generally speaking, prior to 1914, boron crude materials used in Austria and Germany were boracite from Sultan Tchair (Asia Minor) or borate of lime from South America." Thus there is a certain probability that the sample (made prior to 1914) for which Hönigschmid and Birckenbach obtained the value 10·840 was derived from an American source.

The obvious conclusion from our results, thus supported, is that boron from California has an atomic weight, $B = 10·840$, higher by 0·02 than that of boron from Asia Minor, $B = 10·820$. If our interpretation of the results of Series A is correct, the boron from Tuscany ($B = 10·825$) is similar to that from Asia Minor.

These values indicate that the American boron contains 84% and the Eurasian boron 82% of the heavier isotope.

Comparatively few earlier investigations afford any evidence for or against the possibility of such a variation in isotope ratio as is here indicated. Substantially identical results have been found for terrestrial and meteoritic iron, nickel, and cobalt (Iron : Baxter and Thorvaldson, *J. Amer. Chem. Soc.*, 1911, **33**, 337 ; Baxter and Hoover, *ibid.*, 1912, **34**, 1657. Nickel : Baxter and Parsons, *ibid.*, 1921, **43**, 507 ; Baxter and Hilton, *ibid.*, 1923, **45**, 694. Cobalt : Baxter and Dorcas, *ibid.*, 1924, **46**, 357) and in comparing chlorine from sea water with that in several minerals (Mlle I. Curie, *Compt. rend.*, 1921, **172**, 1025) and especially with that in the ancient mineral apatite from Balme (Mlle E. Gleditsch and B. Samdahl, *ibid.*, 1922, **174**, 746).

Brönsted and Hevesy (*Nature*, 1922, **109**, 813) prepared and purified mercury from 9 minerals, from as many different sources

in Europe and America, and compared the densities of these samples : they found no variation greater than the possible experimental error, corresponding to a variation of about 0·0012 in the atomic weight. More recently, Jaeger and Dijkstra (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 393) have compared the densities of samples of tetraethylsilicane prepared from twelve different sources, six meteoritic and six terrestrial, and found no evidence thus of any variation exceeding about 0·001 unit in the atomic weight of silicon.

Munro (J., 1922, **121**, 986) attempted to compare the equivalent weight of borax from the Hanmer Hot Springs, South Island, New Zealand, with that of ordinary commercial borax and could detect no difference. Unfortunately, his work is open to very serious criticism : the weights of borax were very small; the method of ascertaining this weight, by dissolving a *part* of a weighed mass of fused borax and again fusing and weighing the remainder, is objectionable; and the measurement of the *volume* of acid required for neutralisation is insufficiently precise. Further, as we have shown that fused borax is variable in composition, Munro's work must be rejected entirely.

On the other hand, Mlle Curie (*loc. cit.*) has found a value slightly above the normal for chlorine obtained from a Central African desert region, and Muzaffar (*J. Amer. Chem. Soc.*, 1923, **45**, 2009) has reported widely different atomic weights, 121·720, 122·374, 121·563, and 121·144 respectively, for samples of antimony extracted from stibnites from Peru, Bolivia, Borneo, and Hungary. Unfortunately, the method used in the latter determinations seems unsuited to precise work and does not inspire confidence in these results; and the excellent determinations of the ratio $SbCl_3 : 3Ag$ recently published (Sb = 121·77, Willard and McAlpine, *J. Amer. Chem. Soc.*, 1921, **43**, 797; Sb = 121·76, Hönigschmid, Zintl, and Linhard, *Z. anorg. Chem.*, 1924, **136**, 257; Sb = 121·748, Weatherill, *J. Amer. Chem. Soc.*, 1924, **46**, 2437) were made with material of unknown origin and cannot be related to Muzaffar's results.

It would seem that this evidence as a whole may be held to show that there is no inherent improbability in the variation in atomic weight now observed. It remains to be ascertained whether that variation is due to changes in the isotope ratio occurring through processes of solution, fusion, crystallisation, and volatilization occurring in the earth's crust (it may be noted that in most cases boron has probably been concentrated in the existing deposits by volatilisation, as boric acid, in steam), or whether, as Aston has suggested (*Ann. Rep.*, 1922, **19**, 272), the isotope-ratio was fixed at an earlier stage in the history of the element, possibly at the

time of its formation. In the latter case, it is to be anticipated that differences in atomic weight would be most evident, as in the present case, between samples from sources so widely separated in distance that little, if any, admixture can have occurred between them.

Evidently, to answer the question here raised, more, and more precise, data are needed as to the atomic weights of elements from known sources. We therefore urge upon all who determine atomic weights that they should use only materials of definite and known origin and should seek results of the greatest possible precision, so that all such determinations may contribute in some measure to a solution of this fundamental problem of the origin of the elements.

The broad conclusions that may be drawn from this investigation may now be summarised. The present analyses agree with those of Baxter and Scott and of Hönigschmid and Birckenbach in showing that the atomic weight of boron is less than 10·85 and therefore in requiring the rejection, which we have elsewhere justified on other grounds (Briscoe, Robinson, and Stephenson, *loc. cit.*), of all the results based upon the analysis of fused borax. Two samples of boron, derived from Europe and Asia Minor, have atomic weights approximating closely to the rounded mean value *10·82*, in agreement with Hönigschmid and Birckenbach; while a sample of boron derived from North American deposits gives for the atomic weight the rounded mean value *10·84*.

C.—*The Alternation in Molecular Volume of the Normal Monobasic Fatty Acids.*

By WILLIAM EDWARD GARNER and ERIC ALLITT RYDER.

PREVIOUS to this work, no measurements had been made of molecular volumes of the higher aliphatic acids in the solid state, and the published data for these acids in the liquid state were so fragmentary that it was difficult to decide to what extent alternation occurs in this property. Pauly (*Z. anorg. Chem.*, 1921, **119**, 278)

The attached two pages are to be inserted when binding in place of the corresponding two pages sent out with the Journal.

has summarised the known values for the acids with 1 to 8 carbon atoms and claims that a slight, although definite, alteration is observable in the molecular volumes of the liquids at the melting points. This behaviour would, however, be expected, since the melting points are alternating temperatures.

Randall and one of us (J., 1923, **123**, 881) have shown that the heats of fusion of that form of the solid acids stable at the melting point show a marked alternation as the homologous series is ascended (see Fig. 1) and have concluded that this alternation is intimately related to the atomic arrangement of the odd and even acids in the unit crystal cell, the length of which alternates from member to member.

From the work of Müller and Shearer (J., 1923, **123**, 2043, 3152), the unit cell contains 2 mols. of acid arranged end on end with their carboxyl groups in juxtaposition. Of the dimensions of this cell, only a perpendicular length between the carboxyl planes has been definitely established, and this, for the even acids, increases in a regular manner as the length of chain increases by two CH_2 groups. The odd members gave irregular results, very possibly on account of the occurrence of two crystalline forms of these acids which r ndergo transition one into the other comparatively slowly.

Other spacings, *viz.*, 3·7 and 4·1 Å.U., were observed to be the same for both the odd and the even acids, but the significance of these is not clear, no clue being afforded from the X-ray measurements to the actual area of cross section of the unit cell. The volume of the cell cannot at present be calculated without a knowledge of the molecular volumes in the solid state. These molecular volumes together with those for the liquid state have now been determined for the five acids from octoic to lauric (Table I). They are given for 50° for the liquid state, and for 15° for the solid state. For the liquids, a constant increase of 16·8 c.c. per g.-mol. occurs for each CH_2 added to the chain. The temperature coefficient of the molecular volume (Table V) does not change materially from acid to acid; thus, when measured at constant temperature, the molecular volume of the liquids must be a non-alternating property.

For the even acids in the solid state an increment of 27·5 c.c. per $2CH_2$ is obtained; but it will be noted that the molecular volumes of the odd acids in the solid state are greater than the mean of those of the even acids immediately above and below them in the series. Alternation therefore occurs in the molecular volume in the solid state and also in the volume change on fusion. The latter are plotted in Fig. 1 against the number of carbon atoms, and compared with the heats of crystallisation for the same acids. The values of the volume change on fusion lie on two curves, one for the odd

and the other for the even acids.   That for β-undecoic acid lies just
above the curve joining the values for the α-even acids, an analogous
behaviour to that observed previously for the heats of crystallisa-
tion (Garner and Randall, *loc. cit.*).

FIG. 1.

Number of carbon atoms.

• *α-forms.*   ⊙ *β-forms.*

TABLE I.

Acid.	Mol. vol. of liquid in c.c./g.-mol. at 50°.	Δ c.c.	Mol. vol. of solid in c.c./g.-mol. at 15°.	Δ c.c.	d Å.U.	S. sq. Å.U.
Octoic	162·61		140·2		9·5	24·4
Nonoic (a)	179·43	16·82	160·1	19·9	11·45	23·1
Decoic	196·20	16·77	167·8	7·7	11·65	23·8
Undecoic (a)	212·95	16·75	186·5	18·7	12·9	23·9
Lauric	229·84	16·89	195·2	8·7	13·5	23·9
Undecoic (β)			180·0			
Acetic			47·4 *			23·5

* De Visser (*Rec. trav. chim.*, 1893, **12**, 139).

has summarised the known values for the acids with 1 to 8 carbon atoms and claims that a slight, although definite, alteration is observable in the molecular volumes of the liquids at the melting points. This behaviour would, however, be expected, since the melting points are alternating temperatures.

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and the other for the even acids.   That for β-undecoic acid lies just above the curve joining the values for the α-even acids, an analogous behaviour to that observed previously for the heats of crystallisation (Garner and Randall, *loc. cit.*).

FIG. 1.

Number of carbon atoms.

• α-forms.   ⊙ β-forms.

TABLE I.

Acid.	Mol. vol. of liquid in c.c./g.-mol. at 50°.	Δ c.c.	Mol. vol. of solid in c.c./g.-mol. at 15°.	Δ c.c.	Å.U.	S. sq. Å.U.
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Lauric	229·84	16·89	195·2	8·7	13·5	23·9
Undecoic (β)			180·0			
Acetic			47·4 *		3·33	23·5

De Visser (*Rec. trav. chim.*, 1893, **12**, 139).

Area of Cross Section of the Unit Cell.—This may be calculated from the formulæ : (1) $S = MV/6.06d \times 10^{-15}$ sq. Å.U., where d is the length of one molecule in the crystal cell, or from (2) $S = \Delta MV/ 6.06 \times 2.05 \times 10^{-15}$ sq. Å.U., ΔMV being the experimental increment in molecular volume for two CH_2 groups, and 2.05 Å.U. being the length of two CH_2 groups, when measured perpendicularly to the carboxyl planes. Those calculated by the former method (column 7, Table I), employing the experimental values for d of Müller and Shearer (*loc. cit.*) and of Gibbs (J., 1924, **125**, 2622), are identical for both the odd and the even acids within the experimental error of the two sets of figures. Even for acetic acid, of which de Visser (*loc. cit.*) gives values for the solid state, the same value of S is obtained. It thus follows that the area of cross section of the unit cell is a non-alternating property. Calculated by method (2), somewhat lower values are obtained, *viz.*, 22.4, 22.2, and 21.3 sq. Å.U. The cause of the discrepancy between the means of the two sets of figures (means 23.8 and 22.0 sq. Å.U., respectively) is not clear. The experimental errors in the quantities employed in the second calculation, *viz.*, in ΔMV and in the value 2.05 Å.U. for the length of two CH_2 groups, are probably greater than those in method 1. If the value for two CH_2 groups is reduced to 1.9 Å.U., the discrepancy disappears.

The area 23.8 sq. Å.U. is surprisingly large, being greater than the area deduced by Adam (*Proc. Roy. Soc.*, 1922, [*A*], **101**, 463) for the cross section of the molecules of these acids as packed in films on water, *viz.*, 21 sq. Å.U.

The structure of the crystal must be extremely open, if this be the correct cross section for the unit cell.

Calculated Length of the Crystal Cell.—The length of crystal cell containing two molecules, $2d$, may be obtained (1) from the formula $d = MV \times 2.05/\Delta MV$, or (2) from the atomic diameters, $C = 1.54$, $H = 1.15$, and $O = 1.15$ Å.U., respectively (Yardley, *Proc. Roy. Soc.*, 1924, [*A*], **105**, 466), assuming the structures put forward by Müller and Shearer (*loc. cit.*) and later applied by Garner and Randall to the even and α- and β-odd acids. In the calculations made under (2), it has been assumed that the tetrahedral angle for the valencies of the carbon atoms is maintained in all cases. In the detailed analysis which has been made of the possible positions of the atoms in the carboxyl and methyl planes, only one of the possible arrangements for each acid gave a length of chain in agreement with the experimental results of Müller and Shearer. These configurations are given in Fig. 2. It will be seen that the hydrogen atom of the carboxyl group is assumed not to add to the length of chain. The arrangement of the carbon atoms in the chain (not

FIG. 2.

Carboxyl group.
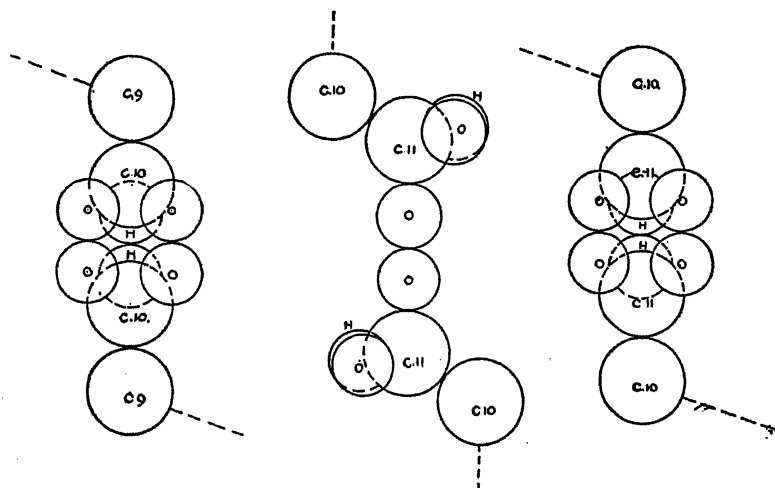
| *Even acid.* | *a-Odd acid.* | *β-Odd acid.* |

Methyl group.
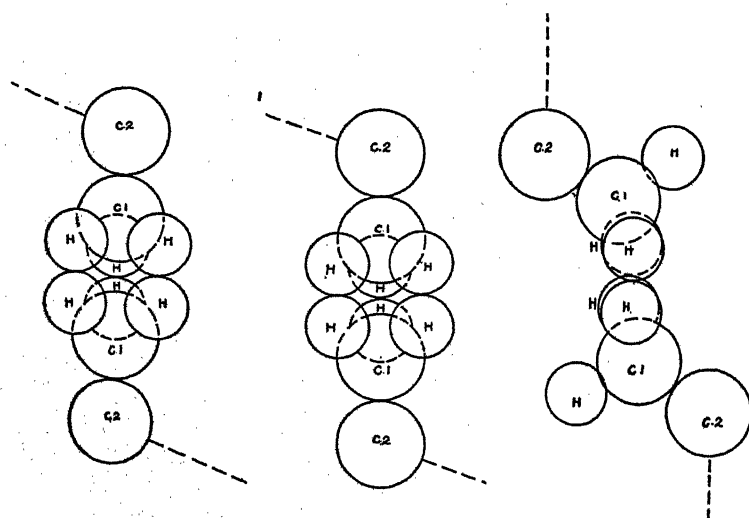
| *Even acid.* | *a-Odd acid.* | *β-Odd acid* |

shown) is such that each $2CH_2$ adds 2·05 Å.U. to the length of the cell. The results obtained by methods (1), (2), and the experimental results of Müller and Shearer, and of Gibbs are given in Tables II

and III.   In the first place, it will be noted that there is a constant difference between the values obtained by method (1) and the experimental results,* but that the latter agree with those obtained by method (2).   If $\Delta 2CH_2 = 2.0$ Å.U., the results by the three methods agree better; but those by the formula $d = MV \times 2.0/\Delta MV$ are still about 0·7 Å.U. too high.   This is practically the half diameter of a hydrogen or oxygen atom, and it is not improbable that a hydrogen atom should be interposed between the two carboxyl groups—Fig. 2, and that the lengths of unit cell, $2d$, given by Müller and Shearer should be increased by the diameter of a hydrogen atom.

Alternation in Length of Chain.—The differences between successive members in the series given in Table II are free from the above objections, as they are the same for both methods of calculation. Thus it will be noted that columns 3 and 5 show good agreement. For the members with 8 to 12 carbon atoms the increase in chain length on passing from an even acid to an α-odd is 1·4 Å.U. and to a β-odd acid 0·8—0·9 Å.U.   Since the differences in column 3 are based on the experimental molecular volumes and those in column 5 on the structures postulated previously (J., 1924, 125, 885) for the α- and β-odd acids in the solid state, the above agreement is an indication that these structures are at least approximately correct. The experimental values of Müller and Shearer and of Gibbs (column 7) are in approximate agreement with these values, but, as it is uncertain which form of the odd acid they employed in their work, a general comparison for the whole series is not possible.

TABLE II.

Length of Chain of Monobasic Fatty Acids.

Acids. No. of carbon atoms.	Method 1.		Method 2.		Experimental.	
	d.	Δ.	*d.*	Δ.	*d.*	Δ.
8	10·45		9·75		9·5	
9 (α)	11·93	1·48	11·15	1·40	11·45	1·95
10	12·51	0·58	11·80	0·65	11·65	0·20
11 (α)	13·90	1·39	13·20	1·40	12·9	1·25
12	14·55	0·65	13·85	0·65	13·5	0·60
10	12·51		11·80			
11 (β)	13·42	0·91	12·61	0·81		

TABLE III.

Length of Chain of Even Acids.

No. of carbon atoms.	2	4	6	8	10	12	14	16	18	20
Experimental (M, S, and G)	3·33	4·83	7·3	9·5	11·65	13·5	16·1	17·35	19·35	23·9
Calculated (Method 2)	3·58	5·63	7·68	9·73	11·78	13·83	15·88	17·93	19·98	24·08

* Nonoic acid is somewhat abnormal.

EXPERIMENTAL.

Materials.—The acids used for the determination of molecular volumes were those employed previously (*loc. cit.*) for the determination of heats of crystallisation. They had the same setting points, with the exception of octoic acid, which had a setting point of 16·20°.

Apparatus.—In the determination of ·the specific volumes, the acid under investigation was placed in the bulb of an air thermometer. The total volume of the bulb empty and the volume of the space not occupied by acid were determined by introducing known volumes of dry air from a gas burette to the evacuated bulb and measuring the resulting pressures. The gas burette, C, and the bulb, B, are shown in Fig. 3. For convenience in handling, the acids were weighed in a glass vessel, A, which made a sliding fit in the bulb, B. The latter was fitted with a carefully ground stopper with a mercury seal and connected with the gas burette and a mercury pump giving a vacuum of 10^{-5} mm. The bulb and burette were rigidly fixed in position in a copper thermostat, and connexion with a mercury manometer, D, was made through one of the sides of the copper tank. The pressures were read by means of a cathetometer supplied by the Cambridge Instrument Company and capable of reading to 1/100 mm.
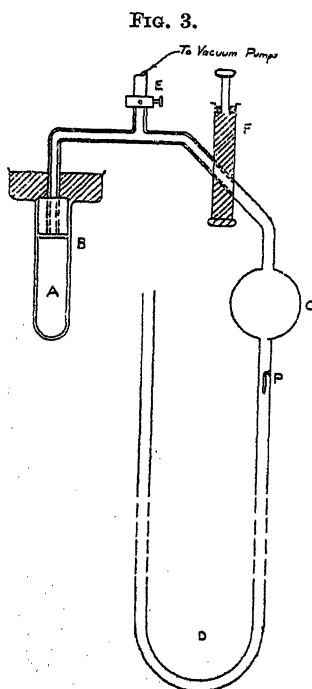
FIG. 3.

Calibration of Gas Burette and Bulb.—The volume of the burette down to the pointer, P, was calibrated by means of mercury, and that of the bulb and its exit tubes by partly filling with a known weight of mercury and determining the remaining free space with air introduced from the burette. The volume of the gas burette was 8·1383 c.c. and that of the bulb 12·9185 c.c. at 19°. The accuracy of these measurements was about 1 part in 4000 and 1 part in 10,000 parts, respectively. Corrections were made for the temperature of different parts of the apparatus, coefficient of expansion of the glass scale and mercury columns, and the usual barometer corrections were made. Since the errors in the specific

volumes were ultimately found to be at least as high as 1 in 500, it is unnecessary to specify the nature of these in detail.

Details of Procedure.—After placing the acid in the bulb of the air thermometer, it was subjected to a preliminary treatment under a vacuum, to remove dissolved air, at a temperature higher than any of the temperatures at which measurements were made. It was then crystallised in a vacuum and cooled to 0°, or below, with the object of producing fine cracks throughout the solid and breaking down any vacuoles that might have been formed. If these precautions were not adopted, erratic results were obtained. Traces of moisture were removed by subjecting the solid to a high vacuum for 2 hours. Since the vapour pressures of the acids under the conditions of the experiments were low, there was no appreciable loss by evaporation; 7·75 g. of octoic acid decreased in weight only 0·0004 g. after a long series of investigations. Before carrying out a measurement, the acid was brought to the required temperature within 0·1°, and a known volume of dry air introduced into the gas burette at about atmospheric pressure, and after it had attained the temperature of the bath, the mercury level was adjusted to the pointer, P, by moving the mercury upwards. Providing no leak developed, the manometer readings, barometric pressure, etc., were then taken. This air was then admitted into the thermometer bulb, the mercury brought up to the pointer, and a reading of the pressure made as soon as possible. Since the equilibrium pressure was not attained until after about 20 minutes, these readings were repeated every few minutes, until no further movement of the mercury was observed. The slow disappearance of air was not due to the same causes in the cases of the liquid and the solid acids. Since the fall in pressure did not occur when the acid was replaced by mercury, it seems clear that the slow change in the case of the liquids was due to solution of air in the surface layers. The value for the volume of the free space, used for the calculation of the specific volume of the liquids, was therefore obtained by extrapolation back to the time of admission of air. The difference in the pressure between the maximum and the initial readings was never more than 2 in 1000, so that the error in the initial reading is unlikely to be large. For the solids, the change in pressure with time was less the more thoroughly the acid was broken up by cooling, thus it cannot be ascribed to absorption on the solid surface. Further evidence in support of this contention was found in the case of undecoic acid, where a complete series of determinations was made during which the equilibrium pressure was attained immediately after admitting the gas. In a number of others, however, the change in pressure was several mm. on a pressure

of about 500 mm. The α-nonoic acid gave the most trouble, and on this account the values for this acid are thought to be less accurate than the others. The change in pressure is most probably caused by the presence of vacuoles which are connected with the surface by a series of fine cracks. Hence the equilibrium pressure was taken for the calculations of the specific volumes in the solid state. The values obtained after melting and resolidifying were identical with those obtained for the first series at the same temperature to within 2 in 1,000.

TABLE IV.

Densities and Specific Volumes (Air Thermometer Method).

Acid.	Wt. (g.).	Temp.	Density.	Specific volume.	Temp. coeff. per 1°.
Octoic	7·7564	10·0°	1·0326	0·9685	0·00098
		15	1·0274	0·9733	
		20	0·9109	1·0979	0·00046
		25	0·9090	1·1002	
Nonoic	7·1509	5·0	0·9952	1·0048	0·00074
		10	0·9916	1·0085	
	7·6853	15	0·9097	1·0993	0·00104
		25	0·9011	1·1097	
Decoic	7·7308	15·0	1·0266	0·9741	0·00085
		25	1·0176	0·9827	
		35	0·8927	1·1202	0·00128
		40	0·8876	1·1266	
Undecoic	7·7713	0·12	1·0431	0·9587	0·00054
		10·0	1·0373	0·9640	
		20	0·9948	1·0052	0·00079
		25	0·9905	1·0096	
		30	0·8907	1·1227	0·00093
		35	0·8871	1·1273	
Lauric	8·3722	35·0	1·0099	0·9902	0·00087
		40	1·0055	0·9945	
		45	0·8767	1·1406	0·00142
		50	0·8713	1·1477	

Results.—The specific volumes were measured at two temperatures for each phase, and from three to five determinations were made at each temperature. At the end of a series over a range in temperatures, the experiments at the first temperature were repeated, and it was found that no drift in the values occurred due to changes in the experimental conditions. To test the method, several series of determinations were made with α-undecoic acid. The means are given in Table IV.

The densities of the acids in the liquid state have also been determined in a pyknometer of volume 5·0470 c.c. at 30°. The experimental results for two temperatures, one as near the melting point as possible, are given in Table V.

Table VI embodies the results obtained by both air thermometer and pyknometer methods for the specific volumes of the solid and

TABLE V.

Acid.	Temp.	Wt. of acid in air (g.).	Density.	Temp. coeff.
Octoic	50·27°	4·4738	0·8862	0·00099
	20·02	4·5923	0·9101	
Nonoic	50·17	4·4491	0·8813	0·00097
	15·00	4·5842	0·9087	
Decoic	50·17	4·4290	0·8773	0·00095
	35·05	4·4834	0·8884	
Undecoic	50·15	4·4129	0·8741	0·00095
	30·00	4·4856	0·8889	
Lauric	50·25	4·3957	0·8707	0·00095
	45·10	4·4140	0·8744	

liquid acids at the melting point and, for the liquid acids, at 50°.
In addition, the change in molecular volume on melting is included.
Those by the air thermometer method have been obtained for each
phase from the results in Table IV, by taking the means for the
two temperatures given, and applying to these values the mean
temperature coefficients given below.

TABLE VI.

		Octoic.	Nonoic.	Decoic.	Undecoic.	Lauric.
Specific volumes.	Solid, M. Pt. (air thermometer).	0·9737	1·0104	0·9870	1·0121	0·9971
	Liquid, M. Pt. (air thermometer).	1·0925	1·0966	1·1169	1·1206	1·1403
	(pyknometer).	1·0951	1·0979	1·1220	1·1232	1·1423
	Liquid 50°. (pyknometer).	1·1283	1·1347	1·1398	1·1440	1·1483
Molecular volumes.	ΔMV at M. Pt.	17·51	13·95	23·24	20·68	29·07

Mean temp. coeff. spec. vol.   Solids : 0·00077 per 1°.
                                Liquids : 0·00103 per 1°.

In calculating the molecular volume change on melting, the
pyknometer values of the liquid acids were used. Those by the air
thermometer method appear to be in error by 2 parts in 1000. The
molecular volume change on melting for β-undecoic acid, assuming
that this acid melts at 28·5°, is 27·26 c.c./g. mol.

Summary.

The molecular volumes of octoic, α-nonoic, decoic, α- and
β-undecoic, and lauric acids have been determined. Those for
the liquid state at 50° increase by 16·8 c.c./g. mol. for each CH_2
group added to the chain, whereas those for the solid state alternate
in a marked manner as the series is ascended. The area of cross
section of one molecule in the crystal, 23·8 Å.U., is non-alternating,
hence the alternation in molecular volume is due entirely to changes
in the chain-length from member to member. The magnitude of
the alternation is in agreement with the views expressed in a

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previous paper (*loc. cit.*) with regard to the constitution of these acids in the solid state.

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CI.—*The Interaction of Nitrogen Sulphide and Sulphur : Nitrogen Persulphide.*

By FRANCIS LAWRY USHER.

IN order to eliminate the last traces of free sulphur from nitrogen sulphide the crystals which separate from benzene * are usually sublimed in a vacuum over a roll of heated silver gauze at steam temperature (Burt and Usher, *Proc. Roy. Soc.*, 1911, [*A*], **85**, 82) On attempting to expedite this process by jacketing the sublimation tube with the vapour of a liquid of higher boiling point than water, namely, *iso*amyl alcohol, b. p. 124—125°/about 695 mm., a ruby-coloured film appeared almost immediately over about 2 feet of the glass tubing connecting the sublimation tube with the mercury pump. At the same time, nitrogen was evolved much more freely than usual, and the silver was rather thickly coated with silver sulphide. The sulphide at the bottom of the sublimation tube, which was subsequently found to be largely contaminated with sulphur, underwent partial fusion, and bubbles of gas or vapour escaped from it. As the sublimation proceeded, the ruby deposit increased in depth of colour, although always retaining its transparency except in the wider tubing just above the cork which fitted into the vapour jacket; on warming, it disappeared, and was condensed on adjacent parts of the tubing as a blue film. After about 2½ hours, the whole of the deposit became deep blue. During the experiment the phosphoric oxide above the pump was coloured a deep pink, whilst the metaphosphoric acid which accompanied it became bluish-green. On the next day, air was admitted to the apparatus, when the colour of the phosphoric oxide turned to a yellowish-red. On treating a portion of the oxide with water, the

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* Crystallisation from carbon disulphide is more effective than crystallisation from benzene in removing sulphur. The best method (apart from sublimation in a vacuum over heated silver gauze) is, however, to shake a solution of the substance in either solvent with mercury for some time.

colour was slowly discharged, and a smell of sulphur dioxide was noticed; whilst from the remainder benzene extracted a small quantity of yellow, crystalline nitrogen sulphide.

This ruby-coloured substance, which was never obtained in quantity sufficient for analysis, was insoluble in all solvents tried, excepting those which altered it chemically, and in fact behaved precisely like the blue nitrogen sulphide described by Burt (J., 1910, 97, 1171). On warming, it turned blue, slowly at 50°, rapidly at 60° ; the product, judged by its appearance and behaviour, being almost certainly chemically identical with Burt's sulphide. No gas was evolved during the conversion of the ruby into the blue substance, and a careful microscopic examination of the tube after the conversion failed to reveal the presence of any other substance beside the blue sulphide : it is therefore concluded that the ruby substance has the same empirical composition as ordinary yellow nitrogen sulphide. The conversion of the ruby to the blue substance at the room temperature (23—30°) sometimes occurred within ½ hour and has never been observed to take more than 2 days.

None of the ruby compound was formed from the same raw material at steam temperature, although on substituting *iso*amyl alcohol for the water the deposit was formed as before, and nitrogen was freely evolved. In the course of a number of similar experiments, the phosphoric oxide was always coloured, but the colour varied : most frequently the oxide nearest to the sublimation tube was red, that next to it blue, the middle portion a pale greyish-blue, whilst the end nearest to the pump was pink.

A sample of nitrogen sulphide re-crystallised from carbon disulphide did not yield any of the ruby compound when sublimed over silver either at steam temperature or at 125°. At 128°, there was a larger yield than usual of the blue sulphide, and a considerable quantity of nitrogen was given off, but no ruby deposit. Finally, a specimen of nitrogen sulphide (0·2 g.) which had been purified by sublimation over silver gauze at steam temperature was re-sublimed at 139°, when only 1 c.c. of nitrogen was evolved, although there was the usual production of blue sulphide without any visible trace of the ruby variety. Two tubes of phosphoric oxide attached to the pump were coloured a deep greenish-blue, which by the next day had changed—without the admission of air—to deep yellow. At 124° only 0·077 c.c. of nitrogen was evolved during the sublimation of 0·25 g., although there was a marked production of the blue sulphide. Attempts to obtain the ruby sulphide from the blue variety were never successful. When an exhausted tube containing the blue sulphide was gradually heated, the substance sublimed unchanged, slowly at 140°, rapidly at 150—160°. At 165°, it was

partly decomposed, yielding a mixture of products among which could be detected two kinds of crystal, probably sulphur and ordinary nitrogen sulphide, together with a smaller amount of a reddish-brown liquid. When the whole tube was heated at 145°, the blue sulphide was all decomposed, yielding the same products as before. On treatment with various indifferent solvents, it either remained unchanged or dissolved in another form : thus in boiling mesitylene it dissolved, forming a yellow solution.

In order to ascertain definitely whether the presence of free sulphur in yellow nitrogen sulphide is necessary for the formation of the ruby product, a mixture of very pure (re-sublimed over silver) nitrogen sulphide with sulphur in the proportion NS : S was sublimed in a vacuum over silver gauze heated at 124—125°; the ruby film was produced just as in the previous experiments.

Nitrogen Persulphide.—The experiment last mentioned was repeated, with the omission of the silver gauze. The mixture of nitrogen sulphide and sulphur fused and emitted bubbles, while a red substance appeared over the tubing leading to the pump, excepting about 6 inches next to the sublimation tube, and condensed especially on portions which were cooled by a pad of wet cotton wool. By local cooling, the red substance, which was liquid, could be distilled from one part of the tubing to another. Nitrogen was freely evolved, although no silver was present. In a subsequent experiment, some of the substance was condensed by means of solid carbon dioxide and alcohol in a small glass bulb carrying two tubes, each of which was drawn down at one place to a capillary. After allowing the sublimation tube to cool so that no more nitrogen was evolved, the apparatus was thoroughly exhausted and the bulb sealed off. Preliminary trials had shown that the red substance could be completely decomposed into nitrogen and sulphur by heating for an hour in the vapour of boiling sulphur, and this method was selected for its analysis. Since only about 0·01 g. could be collected at a time, it was not possible to weigh the compound itself; the glass having to be scratched in order to open the bulb, the small amount of glass powder lost in this way or on breaking the tube would have introduced a relatively large error. To determine the weights of nitrogen and sulphur in an unknown weight of the compound, the sealed bulb was suspended in the vapour of boiling sulphur for 1 hour, after which one of the tubes, the capillary tip of which had been scratched with a glass knife, was attached to a mercury pump by means of a piece of thick-walled rubber tubing, and the system on the pump side of the bulb thoroughly evacuated. The scratched tip was then broken off inside the rubber tubing, and the gaseous contents of the bulb pumped off into a small tube filled

with mercury and inverted over the end of the discharge tube of the pump. This nitrogen was then transferred to a small, constant-volume gas burette and measured. The bulb containing the sulphur was next removed from the pump and both of its tubes were cut off below the capillary tips. It was then weighed on an Oertling assay balance, the sulphur being afterwards burnt out and the bulb weighed empty. The rider used on the assay balance belonged to the set of weight previously used in calibrating the constant-volume burette, and had been calibrated in terms of one of the weights. The following are the results of two analyses made in this way :

Vol. of nitrogen at N.T.P.	1·366 c.c.	1·378 c.c.
Weight of nitrogen	0·001709 g.	0·001724 g.
,, sulphur	0·00786 g.	0·00783 g.
Ratio S : N	2·05	1·98

The empirical formula of the compound is therefore NS_2, and it may conveniently be called *nitrogen persulphide*. The difficulty of collecting it in sufficient quantity precluded the determination of its molecular weight in solution, but some light was thrown on this matter during one of the earlier analyses, when the compound had been heated insufficiently. The nitrogen was collected and measured as already described, but on the next day the surface of the mercury in the constant-volume burette was observed to be slightly soiled, and on re-measuring the nitrogen the volume was found to have diminished by 0·016 c.c. The simplest explanation is that a small proportion of the sulphide had escaped decomposition and had been carried over as vapour with the nitrogen, being subsequently decomposed by prolonged contact with the mercury. In these circumstances, a diminution of volume could occur only if the compound contained one atom of nitrogen in its molecule, and it may therefore reasonably be surmised that the highly diluted vapour at the ordinary temperature has the formula NS_2.

The persulphide is liquid at the ordinary temperature, and has the appearance of bromine, being red in thin films and almost black in layers more than a millimetre thick. At the temperature of solid carbon dioxide it is a pale yellow solid. It can only be distilled without decomposition in a vacuum, and is much more volatile than N_4S_4. It has a penetrating smell, somewhat resembling that of iodine, and is readily soluble in benzene, chloroform, carbon di-sulphide, and ether. An ether solution when mixed with alcoholic potash gives an intense violet colour. It cannot be preserved at the ordinary temperature for more than a day, even in a vacuum, but decomposes slowly into solid products which on examination with a lens appear to be yellow nitrogen sulphide and sulphur. Water decomposes it, giving a mixture of products among which are

ammonium salts and free sulphur. Dry hydrogen sulphide passed into an ether solution produces some separation of sulphur, whilst the originally red liquid becomes almost colourless, and gives with ammonia a yellow precipitate which is soluble in absolute alcohol, but is immediately decomposed by water with separation of sulphur. These reactions could only be observed qualitatively on account of the paucity of material, but they perhaps suggest the formation of an unstable thio-acid of nitrogen.

Mode of Formation of the Volatile Sulphides.—The experiments described in this paper shed no very definite light on the chemistry of the formation of the modifications of ordinary nitrogen sulphide or of the persulphide, although they indicate clearly enough that the former certainly, and the latter possibly, are produced by decomposition of an intermediate compound not yet identified. It has been shown that the ruby sulphide is formed only when free sulphur is present in the yellow nitrogen sulphide, and when this material is sublimed over silver maintained at about 125°; whereas the blue modification is produced over a rather wider range of temperature, and does not require the presence of free sulphur. The view that the persulphide is formed by simple combination is negatived by the observation that nitrogen is freely evolved by the mixture at a temperature at which pure nitrogen sulphide remains quite undecomposed. Either nitrogen sulphide and sulphur interact with the production of the persulphide and nitrogen, or they combine to form a compound which subsequently decomposes into the persulphide and nitrogen. With regard to the blue sulphide, Burt (*loc. cit.*) has pointed out that it arises by the decomposition of a gaseous or at least a very volatile sulphide of unknown composition containing a larger proportion of nitrogen, and this is clearly also the case with the ruby sulphide, which is only formed in the presence of silver, and is always accompanied by a gaseous or very volatile product which reaches and colours phosphoric oxide connected with the sublimation tube by a considerable length of cold tubing. That this volatile substance is formed in appreciable quantity is proved by the possibility of extracting a visible amount of nitrogen sulphide from the phosphoric oxide; and it appears extremely probable that it is not chemically identical with the substance which gives rise to the blue sulphide, for if it were, the production of this or the ruby variety would be determined by conditions at the place where they were deposited rather than by the chemical composition of the parent material. All that can be stated with any confidence is that silver at temperatures from 100° to 140° decomposes ordinary nitrogen sulphide to a very slight extent, forming an unknown volatile product which gives rise to a blue modification; and that a

ruby modification is similarly produced from a different volatile compound which in turn arises by the decomposition by silver, within narrower temperature limits, of another sulphide, which is possibly nitrogen persulphide. There is thus evidence of the existence of at least two volatile sulphides of nitrogen of unknown composition.

Some reference must be made to the remarkable similarity of the properties of nitrogen persulphide to those of the substance prepared by Muthmann and Clever (*Z. anorg. Chem.*, 1897, **13**, 200) by heating a solution of ordinary nitrogen sulphide in carbon disulphide for some hours in a sealed tube, and stated by them to be nitrogen pentasulphide. Muthmann and Clever's substance has been prepared according to their directions, with the object of comparing its behaviour with that of the persulphide, and of attempting to purify it by distillation in a vacuum and analysing the distillate. A " clean " separation from the last traces of solvent by distillation was, however, impracticable with the small quantity of the substance available, and an analysis would therefore have been inconclusive : qualitatively, the resemblance between the two substances was complete. The author would tentatively suggest the possibility of Muthmann and Clever's " pentasulphide " having been a solution of sulphur in persulphide. Apart from the striking similarity in their properties, it may be pointed out that Muthmann and Clever inferred the purity of their material, which was obtained by evaporation of an ethereal solution, from their observation that free sulphur was almost insoluble in ether at the temperature employed by them. If, however, their product was really nitrogen persulphide, there is little doubt that an appreciable quantity of sulphur would have remained in the mixture of the persulphide with ether.

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CII.—*The Interaction of Sodium Chloride and Alumina.*

By FRANCIS HERBERT CLEWS.

SODIUM chloride is known to react with alumina and with silica in a similar manner. Tilghman (Brit. Pat. 11556, 1847), Gossage (*ibid.* 2050, 1862), Hargreaves (*ibid.* 2121, 1867), and Grüneberg and Vorster (*ibid.* 2639, 1874) were aware of the reaction in presence of moisture yielding sodium aluminate and hydrochloric acid, whilst De Lande and Prud'homme (*Bull. Soc. chim.*, 1872, [ii], **17**, 290) and Schultze (*J. pr. Chem.*, 1880, [ii], **21**, 407) observed

the reaction in presence of air or oxygen yielding sodium aluminate and chlorine. The subject was deemed worthy of a more·quantitative investigation.

EXPERIMENTAL.

The heating element consisted of a nichrome-wound silica tube the temperature of which was controlled to $\pm 10°$ over long periods by means of an adjustable resistance in conjunction with an automatic regulator designed to overcome variations in temperature due to fluctuations in the voltage supplied. The furnace temperatures were measured by a standardised platinum–platinum rhodium thermocouple. The reactions were carried out in alundum* tubes which, being somewhat pervious to gases, were enclosed in a slightly larger silica tube.

Products and Course of the Reaction.—The following reactions have been observed :

(a) $4x\text{NaCl} + y\text{Al}_2\text{O}_3 + x\text{O}_2 = 2x\text{Na}_2\text{O},y\text{Al}_2\text{O}_3 + 2x\text{Cl}_2$.

(b) $2x\text{NaCl} + y\text{Al}_2\text{O}_3 + x\text{H}_2\text{O} = x\text{Na}_2\text{O},y\text{Al}_2\text{O}_3 + 2x\text{HCl}$.

(c) $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$.
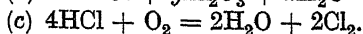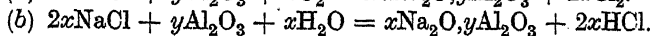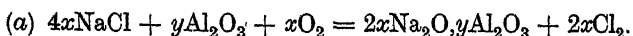
Reaction (b) is reversible at about 1000°. The formation of aluminium chloride has not been observed in these experiments, which have been restricted to reactions in the presence of water. This does not preclude its formation under anhydrous conditions.

Materials.—Pure, dry sodium chloride was used and the alumina was prepared by igniting recrystallised ammonium alum, free from iron, in a muffle, extracting for 2 days in a Soxhlet extractor with dilute hydrochloric acid, re-igniting in the muffle for 6 hours, followed by a fresh extraction for 2 days. The pulverulent product showed no traces of sulphate on testing after fusion with sodium carbonate.

Effect of Rate of Flow of Gas over the Reaction Mixture.—A purified stream of moist air was passed at a constant rate over 0·5 g. of a mixture of equal parts by weight of alumina and sodium chloride placed in a platinum boat and heated in the furnace in a silica-jacketed alundum tube. The gaseous products of the reaction were absorbed in a U tube filled with fragments of glass moistened with sodium bicarbonate and potassium iodide. The reaction tube was finally swept out with a current of dried air. The experiments were duplicated and the results are shown in Table I.

The results indicate that reaction (b) predominates, and that the chlorine produced is to be attributed more to reaction (c) than reaction (a), since it is dependent on the rate at which air and water

* $15·42\%$ SiO_2; $83·25\%$ Al_2O_3; $0·49\%$ Fe_2O_3; $0·52\%$ TiO_2; $0·76\%$ CaO.

TABLE I.

Duration of experiment .... 5 hours.
Mean temperature of furnace .... 1009°.
Temperature of saturation of air with water vapour   50°.

C.c. of air passed.	Cl_2 (c.c. of $N/20$).	HCl (c.c. of $N/20$).	$\dfrac{Cl_2}{HCl}$.	$\dfrac{Cl_2}{HCl + Cl_2}$
9400	10·8	74·6	0·145	0·126
8450	10·5	67·5	0·156	0·135
6500	18·5	63·9	0·290	0·225
3000	24·0	51·6	0·465	0·317
1600	26·2	49·9	0·525	0·344
1250	22·1	35·6	0·621	0·383
1050	17·9	37·4	0·479	0·324

are supplied. Examination of equation (c) shows that a proportionate increase in the concentration of water and oxygen would lead to a displacement of equilibrium to the left.

Effect of Proportion of Sodium Chloride and Alumina.—The results are shown in Table II.

TABLE II.

Duration of experiment .... 5 hours.
Volume of air passed .... 6500 c.c.
Temperature of saturation of air with water ...   50°.
Temperature of furnace .... 1009°.

	HCl (c.c. of $N/20$).	Cl_2 (c.c. of $N/20$).	$\dfrac{Cl_2}{HCl + Cl_2}$
100% NaCl	64·6	16·4	0·202
75% NaCl	76·2	26·0	0·254
50% NaCl	63·9	18·5	0·225
25% NaCl	36·6	6·6	0·150

Effect of Temperature on Reaction (b).—0·5 Gram of an intimate mixture of equal weights of sodium chloride and alumina was heated as previously described in an atmosphere of water vapour produced by allowing water to drip at a very slow constant rate from a capillary tube into the silica tube. The hydrochloric acid produced was collected and titrated with $N/10$-alkali. Reactions (a) and (c) were excluded. The composition of the residue was determined by gravimetric analysis, the sodium oxide being determined by Smith's method (*Amer. J. Sci.*, 1871, [ii], **50**, 269).

At the higher temperature very little of the resulting sodium aluminate was soluble or hydrolysable. The results are summarised in Table III.

The results indicate that above 1000°, for a given quantity of sodium chloride, the reaction with alumina is virtually complete, as would be expected, since the method of supplying the water for the reaction precludes the reverse one.

In these experiments the amount of sodium oxide produced in the platinum boat was always less than that equivalent to the

<div align="center">TABLE III.</div>

Duration of experiment .... 5 hours.

Temp.	HCl (c.c. of $N/10$).	Composition of residue.			$\dfrac{Na_2O}{Al_2O_3}$.
		% NaCl.	% Na$_2$O.	% Al$_2$O$_3$.	
1075°	46·65	0·2	3·7	96·1	0·0385
1008	42·20	0·97	11·8	87·2	0·135
952	35·20	12·1	6·8	81·1	0·0838
897	29·55	—	—	—	—
838	20·30	32·3	5·5	62·2	0·0883
785	8·93	44·6	3·8	51·6	0·0737
707	3·35	—	—	—	—
605	0·50	—	—	—	—

hydrochloric acid absorbed, particularly at the higher temperatures. This is to be attributed to the reaction of sodium chloride vapour with the alundum tube in addition to the reaction of the unvolatilised reagents in the boat. Thus we find that the reaction at 1075°, although productive of the greatest yield of hydrochloric acid, does not give the greatest yield of sodium oxide in the residue.

Equilibrium Experiments.—(A). An attempt was now made to determine the effect of varying proportions of water and hydrogen chloride on the proportion of sodium chloride, sodium aluminate, and alumina in equilibrium with the vapours at a temperature (830°) where sodium chloride is not markedly volatile.

Equilibrium was approached from both sides. In one platinum boat was placed a mixture of equal weights of sodium chloride and alumina, and in another, a mixture of 40% sodium chloride, 40% alumina, and 20% sodium aluminate, made by previously calcining equal weights of alumina and sodium carbonate. The two boats were heated in a stream of water vapour and hydrogen chloride, obtained by allowing a solution of hydrochloric acid to drip slowly through a capillary tube into the silica reaction tube. A blank experiment with an empty tube showed that the acid condensing after passing through the furnace had the same composition as that entering it. The results showed that equilibrium was imperfectly attained in the solid mixtures, since differences of about 1% were obtained in the proportions of sodium oxide present. The results given in Table IV are mean values.

A noticeable feature is the almost constant proportion of sodium oxide in the solid mixture in equilibrium with the gaseous phase, irrespective of the composition of the latter.

(B). Similar experiments were made to ascertain the composition of the sodium aluminate in equilibrium with varying gaseous mixtures of hydrogen chloride and water vapour saturated with sodium chloride vapour at 1045°. The procedure was similar to that just described, but to render the alundum reaction tube inert

TABLE IV.

Mean temperature 829°.

Composition of gaseous phase.	Composition of solid phase.		
$\dfrac{[H_2O]}{[HCl]}$	$\dfrac{[NaCl]}{[Al_2O_3]}$	$\dfrac{[Na_2O]}{[Al_2O_3]}$	$\dfrac{[NaCl]}{[Na_2O]}$
57·4	1·65	0·067	24·6
505·0	1·64	0·080	20·5
2740·0	1·56	0·075	20·8
5480·0	1·53	0·074	20·7

to the gaseous reagents it was first treated with concentrated sodium hydroxide and dried. The boats were then introduced and heating was commenced in an atmosphere of the required composition. Thus the alundum tube as well as the contents of the two platinum boats was finally in equilibrium with the vapours. Equilibrium was assumed to be obtained when the composition of the condensed acid was the same as that of the original, which was usually after 20 to 24 hours' heating. Table V shows the results obtained.

TABLE V.

Mean temperature 1045°.

Composition of gaseous phase $[H_2O]/[HCl]$.					
13·7	27·6	66·9	105·0	529·0	1590·0
Composition of solid phase $[Na_2O]/[Al_2O_3]$.					
0·017	0·026	0·070	0·107	0·102	0·117

The stability of sodium aluminate with reference to hydrochloric acid decreases rapidly at 1045° when the molecular ratio Al_2O_3/Na_2O is less than 10 to 1 (see Table V), and at 830° when the ratio is less than 12 to 1 (see Table IV). In this reaction, no quantitative relationship between the composition of the gaseous phase and of the solid phase is apparent from these results. For the complete reaction of sodium chloride with alumina in the presence of water, an excess of alumina appears to be of greater moment than an excess of water.

CIII.—*A Synthesis of Oxyberberine.** Part I.

By WILLIAM HENRY PERKIN, jun., JANENDRA NATH RÂY, and
ROBERT ROBINSON.

IN view of the recent work of Haworth, Perkin, and Rankin (J.,
1924, **125**, 1686), it cannot be assumed that a synthetical proof of
the constitution of berberine has yet been given and we have
therefore decided to continue the investigation of this subject in
several directions. A simple synthesis of oxyberberine has now
been devised and in the present communication we place this on
record, leaving the more complete description of an intermediate,
at present employed in an unpurified condition, for a subsequent
paper. Meconinecarboxylic acid (I) was synthesised by Fritsch
(*Annalen,* 1898, **301**, 358) from *o*-veratric acid, and a simple method
of preparation from opianic acid has been indicated by Robinson and
Robinson (P., 1913, **29**, 267). The latter method was employed by
Freundler (*Bull. Soc. chim.,* 1914, [iv], **15**, 465), who prepared
numerous derivatives of the acid and among these the β-piperonyl-
ethylamide (II), m. p. 148°.
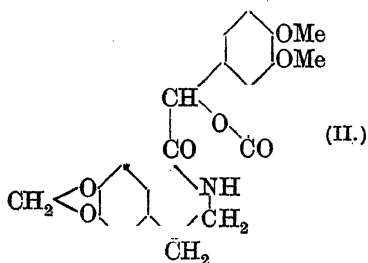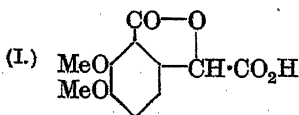
According to Freundler this substance is not converted into a
dihydro*iso*quinoline derivative by the action of phosphoric anhydride
or phosphoryl chloride, and we can confirm this statement if the
treatment is of short duration. We found, however, that change
did occur when the amide in phosphoryl chloride solution was
heated during some hours on the steam-bath, and on adding the
product to water an ochreous precipitate was obtained. This was to
a large extent insoluble in boiling acetic acid, and the pale yellow
residue, which could be crystallised from hot aniline, showed the
highly characteristic reactions and properties of dioxyberberine
(III) (Perkin, J., 1889, **55**, 1087).

This experiment was a preliminary trial and was made merely to
determine whether reaction occurred at all. The conditions are not
precisely known and on repetition, with larger amounts but in
similar circumstances in other respects, different results were

* Compare Pictet and Gams. *Ber.,* 1911, **44**, 2036.

obtained. The neutral product was produced in small relative amount and was not dioxyberberine, whilst the main product was a

(III.)

$$\begin{array}{c} \text{OMe} \\ \text{OMe} \\ \text{HO·C} \\ \text{C} \quad \text{CO} \\ \text{CH}_2 \overset{O}{\underset{O}{<}} \quad \text{N} \\ \text{CH}_2 \\ \text{CH}_2 \end{array}$$

(IV.)

$$\begin{array}{c} \text{OMe} \\ \text{OMe} \\ \text{CH} \quad O \\ \text{C} \quad \text{CO} \\ \text{CH}_2 \overset{O}{\underset{O}{<}} \quad \text{N} \\ \text{CH}_2 \\ \text{CH}_2 \end{array}$$
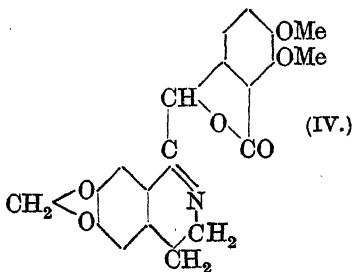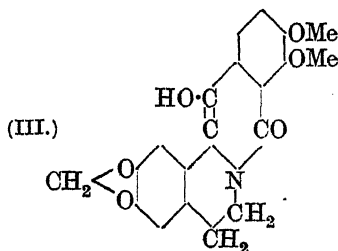
base which we regard as a dihydro*iso*quinoline (IV), although this is at present only a working hypothesis. When the entire basic product was treated with zinc dust in boiling acetic acid solution, oxyberberine (VI) was produced, possibly through the intermediate (V). Naturally the mechanism of the whole process will be further closely investigated, but whether the explanation which we now advance is subsequently justified or not, the synthesis establishes the correctness in important details of the constitution now generally assumed for oxyberberine and, in particular, a satisfactory proof of the position of the methoxyl groups is afforded.

(V.)

$$\begin{array}{c} \text{OMe} \\ \text{OMe} \\ \text{CH} \quad O \\ \text{CH} \quad \text{CO} \\ \text{CH}_2 \overset{O}{\underset{O}{<}} \quad \text{NH} \\ \text{CH}_2 \\ \text{CH}_2 \end{array}$$

(VI.)

$$\begin{array}{c} \text{OMe} \\ \text{OMe} \\ \text{CH} \\ \text{C} \quad \text{CO} \\ \text{CH}_2 \overset{O}{\underset{O}{<}} \quad \text{N} \\ \text{CH}_2 \\ \text{CH}_2 \end{array}$$
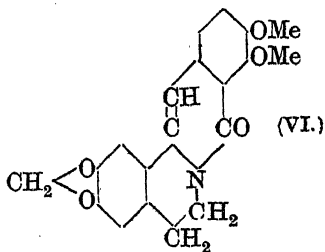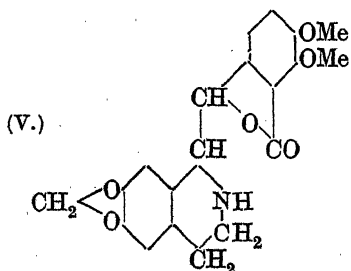
A synthesis of oxyberberine is also a synthesis of tetrahydroberberine and therefore of berberine, because oxyberberine has been shown to yield tetrahydroberberine when reduced electrolytically (Perkin, J., 1918, **118**, 764). Moreover, berberine is the starting point for the syntheses of other alkaloids, for example, canadine (Gadamer and Voss, *Arch. Pharm.*, 1910, **248**, 43) and palmatine (Späth and Lang, *Ber.*, 1921, **54**, [*B*], 3064).

EXPERIMENTAL.

Meconinecarboxylic Acid (I) *and its* β-*Piperonylethylamide* (II).— A mixture of opianic acid (20 g.), pure potassium cyanide (8 g.), and water (75 c.c.) was allowed to remain during 40 minutes and,

after the addition of 15% hydrochloric acid (60 c.c.), boiled during 12 minutes. α-Cyanomeconine (Robinson and Robinson, *loc. cit.*) separated from the hot solution as an oil, which readily crystallised on cooling the liquid. The substance was collected, washed with water, and hydrolysed by boiling with concentrated hydrochloric acid (60 c.c.) during 2 minutes. The liquid was diluted with water and, on standing, meconinecarboxylic acid crystallised (14 g. and 3—4 g. from the mother-liquor) from the solution. The substance was recrystallised from benzene or from water. The pure acid (10 g.) (dried in a vacuum at 78°) was covered with dry benzene (20 c.c.), and purified thionyl chloride (20 c.c.) added, the mixture being then gently warmed until evolution of hydrogen chloride appeared to have ceased. The volatile materials were then removed by distillation in a vacuum below 100° and the residue was once more warmed with thionyl chloride (20 c.c.) and isolated in the same manner as before. The crude acid chloride, completely freed from thionyl chloride, was dissolved in benzene (100 c.c.) and gradually added to a dry benzene solution of β-piperonyl-ethylamine (prepared from 20 g. of the hydrochloride). After remaining over-night, the mixture was heated on the steam-bath for 15 minutes, cooled, and filtered. The precipitate was washed with dilute hydrochloric acid, whilst the benzene solution was washed with hydrochloric acid and aqueous sodium carbonate and evaporated. The desired amide, m. p. 148°, was obtained both from the separated solid and from the solution, and after crystallisation from alcohol 9 g. of the pure substance were obtained, whilst 3 g. were subsequently recovered from the alcoholic mother-liquor.

Oxyberberine.—Meconinecarboxy-β-piperonylethylamide (4·5 g.) and freshly distilled phosphoryl chloride (45 c.c.) were heated together on the steam-bath during 5 hours. The mixture was decomposed by means of crushed ice, and the liquid filtered, leaving a small residue (A). The bright yellow filtrate and washings (totalling about 700 c.c.) were rendered faintly alkaline with sodium hydroxide, when an ochre-yellow base was precipitated. The substance was collected, well washed with water, and dried in the air. This base becomes crystalline in contact with alcohol, but some change appears to occur when it is treated with the hot solvent and we have not yet obtained the compound in a pure condition. The entire crude basic product from the experiment described above was mixed with zinc dust (10 g.) and acetic acid (50 c.c.), the mixture boiled during 5 minutes, a second equal portion of zinc dust was then added, and the boiling continued for 25 minutes. The cooled solution was diluted with a relatively large volume of ethyl acetate, filtered, and washed several times with dilute hydrochloric acid,

then with aqueous sodium hydroxide and with water. The solution was dried by means of potassium carbonate, filtered, and the solvent removed by distillation. The yellow, crystalline residue was mixed with alcohol (20 c.c) and after the addition of sodium hydroxide (2 g.) in water (5 c.c.) the whole was heated on the steam-bath during 5 minutes. The flocculent precipitate obtained on the addition of water was now free from the original amide, with which a specimen, obtained in an earlier experiment, was found to be contaminated. The substance was collected, washed, dried at 100° (0·6 g.), and crystallised successively from alcohol, xylene, and alcohol. The woolly needles change in contact with the solvent into rather larger, pale yellow, flat needles, m. p. 198—200° (Found :*N = 4·16. Calc. for $C_{20}H_{17}O_5N$, N = 3·99%). The melting point of oxyberberine given by Perkin (*loc. cit.*, p. 1085) is 198—200°, and this is certainly the value obtained if the substance is submitted to ordinary processes of purification. An exceptionally pure specimen was, however, obtained by crystallisation as the acetate, then as free base from ethyl acetate and alcohol. This product was used in an attempt to reduce the substance by means of zinc dust and hydrochloric acid in alcoholic solution; it was recovered and thrice crystallised from xylene and once from alcohol. The nearly colourless needles melted at 200—201° and a mixture with the synthetical specimen melted at 199—200°. We have also mixed the synthetical material with an ordinary authentic specimen of oxyberberine, m. p. 198—200°, and observed no depression of the melting point. The behaviour of the synthesised material with solvents, its habit of crystallisation, and the form of the crystals, were identical with the corresponding properties of oxyberberine. The bluish-violet fluorescence in neutral organic solvents, which is bright in the light of burning magnesium, was identical with that exhibited by oxyberberine, and the characteristic reaction of the substance with 50% sulphuric acid and a drop of nitric acid (giving an intense violet colour and a permanganate-coloured precipitate on dilution with water) was identical in the case of both specimens. The acetate derived from the synthetical specimen crystallised from acetic acid in hexagonal tablets.

The residue (A) was dissolved in hot glacial acetic acid and, on cooling, a small amount of yellow crystals separated. The substance was several times recrystallised from acetic acid, in which it was sparingly soluble, and obtained as a crust of yellow needles, m. p. 230°, and containing chlorine. The substance shows

* We are indebted to Mr. J. C. Smith, M.Sc., for carrying out this microanalysis by the Pregl-Dumas method.

the characteristic reactions of methyl*nor*oxyberberine * (Faltis, *Monatsh.*, 1910, **31**, 557), m. p. 245°, but it depresses the melting point of this substance when mixed with it and is probably a chloro-methyl*nor*oxyberberine derived from dioxyberberine by replacement of a hydroxyl group by a chlorine atom accompanied by demethylation. In the course of our further work we hope to collect sufficient of this substance to enable us to characterise it by analysis.

THE UNIVERSITIES OF OXFORD
    AND MANCHESTER.   [*Received, February 16th,* 1925.]

CIV.—*The Surface Tensions of Aqueous Solutions of Various Organic Compounds.*

By PERCIVAL ROWLAND EDWARDS.

DURING the course of work on adsorption at air-liquid interfaces it became necessary to make determinations of the surface tension of aqueous solutions of different organic compounds. The method proposed by Ferguson (*Trans. Faraday Soc.*, 1921, **16**, 384) was adopted, as apparently the soundest from a theoretical point of view. This method consists in dipping a capillary tube, of known diameter, for some small portion of its length into the liquid whose surface tension is to be determined, and measuring the pressure required to force the liquid down in the capillary tube until the meniscus is flat and just level with the end of the capillary.

The pressure was exerted by raising and lowering a water reservoir and was measured by means of a paraffin manometer, which was read by a cathetometer reading to 0·005 mm. The mean of four pressure readings was taken in each case. The depth at which

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* *Correction.*—Having had occasion to prepare methyl*nor*oxyberberine, $C_{19}H_{15}O_5N$, by the method of Faltis (*loc. cit.*), we were struck by its resemblance to the *iso*oxyberberine of Bland, Perkin, and Robinson (J., 1912, **101**, 262) and found, on making a direct comparison, that the substances are indeed identical. The name *iso*oxyberberine has therefore no longer any significance. Careful fresh analyses have confirmed the view of Faltis in regard to the composition of the compound (Found : C = 67·5, 67·8, 67·5; H = 4·6, 4·7, 4·5. $C_{19}H_{15}O_5N$ requires C = 67·6; H = 4·5. $C_{20}H_{17}O_5N$ requires C = 68·4; H = 4·8%). Methyl*nor*oxyberberine is derived from oxyberberine by hydrolysis of one methoxyl group, but we have not found it possible to reconvert the phenol into oxyberberine by vigorous treatment with methyl sulphate and methyl-alcoholic potassium hydroxide (Found, in recovered material : MeO = 8·9. $C_{19}H_{15}O_5N$ containing 1MeO requires MeO = 9·2%). The properties of methyl*nor*oxyberberine and its relation to oxyberberine will be further investigated.—W.H.P., R.R.

the capillary tube was immersed in the liquid was kept constant by means of a pointer, fused to the side of the tip and just touching its own image on the surface of the liquid.

The radius of the capillary tube at its tip and the distance of the pointer from the end of the tube were determined by means of a microscope eyepiece scale, which was calibrated against a Zeiss standard subdivided millimetre scale. The mean of six readings was taken in each case. The radii of the two capillary tubes used were (A) 0·0194 cm. and (B) 0·0225 cm. and the distance of the pointer from the capillary tip was (A) 0·180 cm., (B) 0·120 cm.

The capillary tube, when not in use, was kept in dichromate solution. Prior to use, it was rinsed several times with water, then with alcohol, and finally with water and the solution to be used. The solution was contained in a plane-sided glass cell (5 cm. cube, mounted on a stand with fine screw adjustment). The whole apparatus was placed in a small chamber the temperature of which was constant to within $\pm$ 0·02° during an experiment.

The surface tension of a solution was calculated by means of the expression

$$\gamma = gr/2 \cdot (\rho_1 h_1 - \rho_2 h_2) + g\rho_2 r^2/6,$$

where $r =$ internal radius of the capillary tube at the tip; $h_1 =$ pressure in cm. of paraffin; $\rho_1 =$ density of the paraffin in g./c.c. = 0·8112 g./c.c. at 16·0°; $h_2 =$ distance between the pointer and the tip = depth of immersion of the tip in the solution; $\rho_2 =$ density of the solution in g./c.c. (in these cases always very nearly unity).

The solutions were made by dissolving weighed quantities of the substances in boiled-out, distilled water and diluting the solutions to 100 c.c. The more dilute solutions of amyl alcohol, menthol, camphor, and thymol in water were made by diluting stronger solutions prepared as described above. The highest concentrations approached the limits of solubility of the substances used.

TABLE I.

Surface tension (γ in dynes per cm.) of aqueous solutions. Concentrations (c) are in g. per 100 c.c. of solution. Tube A.

Merck's pure amyl alcohol redistilled, b. p. 137·8°.

$t°$ ...	15·0	16·0	15·0	16·0	15·0	15·0	15·0	15·0	15·0
c ...	2·000	1·000	1·000	0·500	0·500	0·250	0·250	0·125	0·000
γ ...	35·35	43·68	44·16	53·04	53·14	59·91	59·85	65·38	75·10

The following three, menthol, camphor, and thymol, were studied on account of the well-known peculiar behaviour of their crystals when placed on a water surface.

Menthol (British Drug Houses), m. p. 215·6°.

$t°$	16·0	16·0	16·0	15·0	15·0	
c	0·0000	0·0005	0·0011	0·0021	0·0043	
γ	75·00	74·76	74·37	72·36	69·34	

Camphor (British Drug Houses), m. p. 176·0°.

$t°$	17·0	17·5	17·0	17·0	17·0	16·5
c	0·0000	0·0135	0·0271	0·0542	0·1083	0·2166
γ	74·89	74·59	74·45	73·80	72·74	71·96

Thymol (British Drug Houses), m. p. 49·7°.

$t°$	17·5	17·5	17·5	18·0	18·0	18·0
c	0·0000	0·0034	0·0068	0·0125	0·0250	0·0500
γ	74·81	73·61	71·51	67·53	61·80	55·54

It is evident, therefore, that the " dancing " of these substances, familiar in the case of camphor when placed on the surface of water, is due to the lowering of the surface tension. A crystal of *p*-toluidine " dances " more vigorously than any of the above.

The surface tensions of aqueous solutions of the following substances also were measured.

TABLE II.

Surface Tension of Aqueous Solutions of Various Organic Compounds.

Substance.	Source.	Tube.	Temp.	c.	γ.
Phenacetin	B.D.H.	A	16·0°	0·1080	72·81
Camphoric acid	,,	,,	,,	0·5852	57·33
		,,	,,	0·6500	55·69
		,,	,,	0·6500	56·04
Aceto-*p*-toluidide	,,	,,	,,	0·1000	72·48
		,,	17·0	0·1000	72·18
Piperonal	,,	,,	,,	0·1600	72·83
		B *	,,	0·1600	72·83
Hippuric acid	,,	A	16·5	0·3000	74·27
		B	,,	0·3000	74·53
Ethyl succinate	Merck	,,	18·0	1·5966	48·11
Methyl salicylate	,,	,,	16·0	0·3600	67·18
Ethyl malonate	Kahlbaum	,,	17·0	1·9636	49·53
Salicylic acid	,,	,,	14·5	0·1400	71·41

* Tube B gave $\gamma = 75·09$ and $\gamma = 74·$: for water at 15·0° and 17·0° respectively.

A series of accurate determinations was also carried out with solutions of well recrystallised *p*-toluidine (Kahlbaum, m. p. 45·6°; solubility 0·654 g. in 100 c.c. of water at 15·0°).

Each surface tension reading was obtained by taking the mean of six pressure readings.

The form of the surface tension–concentration curves is highly individual; *e.g.*, that for *p*-toluidine, showing a point of inflection, is in striking contrast to that for amyl alcohol. In all cases, however, the surface tension tends to approach a constant value,

TABLE III.

Surface Tensions of Aqueous Solutions of p-*Toluidine.*

Tube.	Temp.	c.	γ.	Tube.	Temp.	c.	γ.
A	17·0°	0·0000	74·90	A	16·0°	0·1300	65·98
,,	,,	0·0000	74·83	B	,,	0·1500	65·14
B	16·0	0·0200	74·50	A	16·5	0·1600	62·65
A	,,	0·0300	74·44	,,	16·0	0·1800	61·31
,,	,,	0·0600	73·33	,,	16·5	0·2250	58·22
,,	,,	0·0600	73·31	,,	16·0	0·3000	54·43
B	17·0	0·0700	73·13	,,	17·5	0·3000	53·27
A	,,	0·0800	71·97	,,	15·5	0·3000	54·61
,,	,,	0·1000	69·63	,,	16·0	0·3600	50·15
,,	16·5	0·1000	69·67	,, *	,,	0·4500	47·41 *
B	15·0	0·1100	69·39	,, *	17·0	0·6000	42·31 *
A	16·0	0·1200	67·57	,, *	,,	0·6000	42·44 *

* In almost saturated solutions it became difficult to obtain accurate readings owing to excessive " stickiness " and " foaming."

although this is not attained even in saturated solution.* Although all the substances are crystalloids, the lowering of the surface tension is comparable with that of the most active colloids.

A number of other substances, such as phenyldimethylcarbamide, phenylacetanilide, erucic acid, salol, p-cresol, and isoamyl valerate, were investigated, but owing to their very low solubility in water, quantitative readings were not taken. The last-named substance remains on a water surface in the form of droplets which " dance " in a similar manner to camphor.

In all cases the relative lowering of the surface tension of water by these organic compounds can be readily explained on the basis of the Harkins-Langmuir theory of " polar " molecules and surface tension.

* If, as seems possible, the surface layer of a solution containing a very readily adsorbed substance always becomes covered with a monomolecular film of solute when saturation concentration is approached, the surface tension should approach a constant value in each case. This would explain the tendency of surface-tension curves to become parallel to the concentration axis as saturation is approached. With a view to test this conclusion, Mr. G. P. Davies has made measurements with a Du Nouy tensimeter. At least 15 secs. were allowed for the surfaces to age. For water and solutions containing 0·45, 0·60, and 0·65 g., respectively, of p-toluidine the surface tensions found were 73·2, 53·7, 51·4, and 51·8 dynes per cm. These results support the suggestion here put forward.

CV.—*Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. Part IV. The Influence of Substitution in the Amide Group on the Reactivity of the Halogen Atom in Bromomalonamide.*

By RALPH WINTON WEST.

IN Part II of this series (J., 1922, **121**, 2196), it was shown that substitution in the amide groups of malonamide markedly affects the ease of halogenation of the malonyl methylene group, steric rather than polarity factors being the determining influence. In the investigation of such a problem, however, it is essential to consider not only the ease of introduction of the halogen atom, but also the ease of its removal. By the estimation of the velocity coefficient of the reaction :CHBr + HI = :CH$_2$ + IBr, already discussed (J., 1924, **125**, 710), it has been possible to study the effect of the presence of some commonly occurring groups on the reactivity of the bromine atom. In order thoroughly to test the effects of the groups, the compounds were as far as possible considered in sets of three, (I) R'·CO·CHBr·COR', (II) R''CO·CHBr·COR'', (III) R'CO·CHBr·COR'', such that III is the compound intermediate between I and II.

Velocity coefficients at 25°.

R'.	R''.	k_1.	k_2.	k_3.	Calc. k_3
NH$_2$	NHEt	0·81	1·1	0·93	0·87
,,	NHPr$^\beta$	,,	1·5	0·95	1·00
,,	NH·C$_4$H$_9$ (*iso*)	,,	1·6	1·12	1·03
,,	NH·C$_6$H$_4$Me (*p*)	,,	17·5	3·15	3·21
NHMe	,,	1·01	,,	3·99	3·91
NHEt	,,	1·12	,,	4·34	4·29
NHPr$^\beta$	,,	1·50	,,	5·57	5·58
NH·C$_4$H$_9$ (*iso*)	,,	1·60	,,	5·87	5·92
NH·CH$_2$Ph	,,	(1·63)	,,	6·04	—
OH	,,	—	,,	9·6	—
OEt	,,	—	,,	13·3	—
NHEt	NHPr$^\beta$	1·12	1·5	1·42	1·34
NH$_2$	NH·C$_6$H$_4$Br (*p*)	0·81	(80)	6·61	—
NHMe	,,	1·01	(79)	8·0	—
NHEt	,,	1·12	(85)	9·11	—

The figures given in the column headed k_3 (calc.) are obtained by means of the formula $\log k_3 = 0{\cdot}9 \log k_1 + 0{\cdot}474 \log k_2$, where $k_2 > k_1$. This formula is empirical, but gives results in good agreement with those found by experiment, suggesting that, although the mathematical basis of the problem is not understood, yet it should be relatively simple in character. The figures in brackets also are calculated, experimental difficulties making direct estim-

ation impossible.   The three values so obtained for bromomalon-*p*-bromoanilide are in fair agreement with one another, but are probably too high, as the figure is outside the range of the experimental expression.

From this table it is possible to arrange the groups in ascending order of their effect on the reactivity of the bromine atom :

NH_2, NHMe, NHEt, $NHPr^\beta$, $NH \cdot C_4H_9(iso)$, $NH \cdot CH_2Ph$, OH, OEt, $NH \cdot C_6H_4Me(p)$, $NH \cdot C_6H_4Br(p)$.

By an extension of the steric explanation of Chattaway and Harrison (J., 1916, **109**, 172), whereby an increase in the groups R′ and R″ would tend to decrease the solid angle occupied by the bromine atom and so increase its reactivity, the order of the groups could be explained with the exceptions of OH and OEt, which are too high in the series.   As, in considering steric relationships, the configuration of the groups must be taken into account in addition to their additive molecular volumes, it is possible to conceive that *iso*butyl and benzyl have very similar steric volumes. The sudden rise, however, in the case of *p*-tolyl requires explanation.

$$\text{(IV.)} \qquad \begin{matrix} C_7H_7 \cdot NH \cdot CO \\ \\ NH_2 \cdot CO \end{matrix} \!\!\!\diagdown_{\!\theta}\!\! C \diagdown^{OH}_{OH} \qquad\qquad \begin{matrix} C_7H_7 \cdot NH \cdot CO \\ \\ C_7H_7 \cdot NH \cdot CO \end{matrix} \!\!\!\diagdown_{\!\theta}\!\! C \!=\! O \quad \text{(V.)}$$
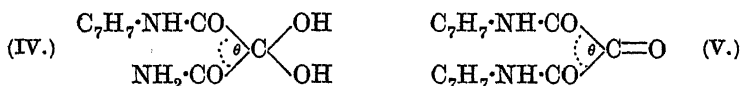
Plowman and Whiteley (J., 1924, **125**, 587) have shown that mesoxmono-*p*-tolylamide is more stable in the dihydroxy-form (IV), and that mesox-*p*-toluidide is more stable in the keto-form (V).   Having regard to the fact that mesoxalic ester exists in the dihydroxy-form, it is necessary to base the explanation on steric factors, and not on polarity effects.   The authors suggest that the increase in θ in passing from (IV) to (V) would cause congestion of the hydroxy-groups and a tendency to form a stable double linking. In the closely related bromomalonyl compounds it would be expected to follow that the steric effects of the para-substituted phenyl groups would be correspondingly large.

From the polarity theory put forward by Lapworth (*Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 10), and the electronic theory of J. J. Thomson (*Phil. Mag.*, 1923, [vi], **46**, 497), it would be expected that OH and OEt would bring about the greatest increase in the reactivity of the bromine atom.   This might account for the high position of these groups in the sequence, but it is only one of several directions in which an explanation of the relative effects of the OX and NHX groups is to be sought.

Thus it would appear that the influence of a group on the reactivity of the halogen atom in this series of compounds is some function of the electronic and steric effects of the group.

Some of the velocity coefficients were also measured at 30·2°. The results are readily correlated by an empirical expression similar to that used for the results at 25°, *viz.*, $\log k_3 = 0.7 \log k_1 + 0.522 \log k_2$. The variation of the temperature coefficients suggests that the reaction proceeds in several stages, each of which is controlled by a separate energy equation.

EXPERIMENTAL.

*Malondi*isopropylamide.—A mixture of ethyl malonate (9·5 g.) and *iso*propylamine (7 g.) was heated in a sealed tube at 120° for 2 hours and at 160° for 7 hours. The alcohol was removed and the solid crystallised from petroleum, separating in needles (9 g.), m. p. 114° (Found : N = 15·13. $C_9H_{18}O_2N_2$ requires N = 15·07%).

Malonmonoethylamide.—Ethyl malonamate (5 g.) was mixed with excess of monoethylamine solution, and kept for 24 hours. After evaporation to dryness, the product separated from alcohol-benzene in plates (4·5 g.), m. p. 123° (Found : N = 21·65. $C_5H_{10}O_2N_2$ requires N = 21·54%).

*Malonmono*isopropylamide.—A mixture of ethyl malon*iso*propylamate and excess of ammonia solution was kept for 48 hours. After evaporation, the product separated from alcohol–benzene in prisms, m. p. 129° (Found : N = 19·60. $C_6H_{12}O_2N_2$ requires N = 19·44%).

*Malonmono*isobutylamide.—A mixture of ethyl malonate (12 g.) and *iso*butylamine (5 g.) was heated in a sealed tube for 24 hours at 100°. The alcohol was removed on the water-bath, the resulting deliquescent solid allowed to absorb moisture, and the malondi-*iso*butylamide filtered off. The filtrate was mixed with excess of ammonia solution, and kept for 24 hours. The solid obtained on evaporation was dissolved in 5 c.c. of alcohol, the solution well cooled, and the malonamide filtered off. The *malonmonoisobutyl-amide* obtained on evaporation separated from benzene in needles, m. p. 83° (Found : N = 17·81. $C_7H_{14}O_2N_2$ requires N = 17·72%).

*Malonmonoethylmono*isopropylamide, $NHEt \cdot CO \cdot CH_2 \cdot CO \cdot NHPr^\beta$, obtained by condensing ethyl malon*iso*propylamate with mono-·ethylamine, separated from petroleum in needles, m. p. 98° (Found : N = 16·21. $C_8H_{16}O_2N_2$ requires N = 16·29%).

Malonmonomethylmonophenylamide, m. p. 151° (Found : N = 14·50. $C_{10}H_{12}O_2N_2$ requires N = 14·58%), and *malonmonoethyl-monophenylamide*, m. p. 154° (Found : N = 13·71. $C_{11}H_{14}O_2N_2$ requires N = 13·59%), were each prepared by allowing ethyl malonanilate to stand in contact with a solution of the corresponding amine for 24 hours. In each case, the product was extracted with

boiling water, the required product separating from the solution on cooling.

Malonmonomethylmono-p-*tolylamide*, m. p. 183° (Found : N = 13·70. $C_{11}H_{14}O_2N_2$ requires N = 13·59%), and *malonmonoethyl-mono*-p-*tolylamide*, m. p. 176° (Found : N = 12·68. $C_{12}H_{16}O_2N_2$ requires N = 12·73%), were prepared similarly to the corresponding phenyl compounds, and separated from water in plates.

Malonmonoisopropylmono-p-*tolylamide*, m. p. 192° (Found : N = 11·90. $C_{13}H_{18}O_2N_2$ requires N = 11·97%), *malonmonoiso-butylmono*-p-*tolylamide*, m. p. 177° (Found : N = 11·39. $C_{14}H_{20}O_2N_2$ requires N = 11·29%), and *malonmonobenzylmono*-p-*tolylamide*, m. p. 188° (Found : N = 10·07. $C_{17}H_{18}O_2N_2$ requires N = 9·93%), were each prepared by heating ethyl malon-*p*-toluidate with the corresponding amine in a sealed tube at 120° for 4½ hours. They separate from alcoholic solution in needles.

Bromination of the Substituted Malonamides. General Methods.
—(1) For those compounds containing the phenyl group, the general formula for the brominated product being

$$R\cdot NH\cdot CO\cdot CHBr\cdot CO\cdot NH\cdot C_6H_4Br(p).$$
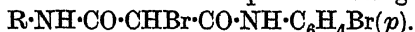
The amide (1 mol.), dissolved in hot acetic acid, was slowly treated with a solution of bromine (2 mols.) in the same solvent. The solvent was removed at the room temperature, the product treated with a small quantity of ether, and filtered.

(2) For compounds not containing the phenyl group, the general formula for the brominated product being

$$R'\cdot NH\cdot CO\cdot CHBr\cdot CO\cdot NHR''.$$
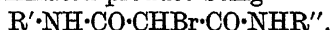
The procedure was as described in (1), except that one mol. of bromine was used. Several of the compounds yielded syrups, but these were readily rendered solid by repeated treatment with small quantities of petroleum (b. p. 40—60°).

Bromomalondiisopropylamide, m. p. 204° (Found : Br = 30·02. $C_9H_{17}O_2N_2Br$ requires Br = 30·16%), *bromomalonmonomethylmono-*p*-bromophenylamide*, m. p. 187° [Found : Br (malonyl) = 22·56. $C_{10}H_{10}O_2N_2Br_2$ requires Br (malonyl) = 22·85%], *bromomalonmono-methylmono*-p-*tolylamide*, m. p. 186° (Found : Br = 27·90. $C_{11}H_{13}O_2N_2Br$ requires Br = 28·07%), *bromomalonmonoethylmono-*p*-tolylamide*, m. p. 178° (Found : Br = 26·60. $C_{12}H_{15}O_2N_2Br$ requires Br = 26·73%), and *bromomalonmonobenzylmono*-p-*tolyl-amide*, m. p. 167° (Found : Br = 22·02. $C_{17}H_{17}O_2N_2Br$ requires Br = 22·14%), all separate from alcohol in needles. *Bromomalon-monoethylamide*, m. p. 161° (Found : Br = 38·41. $C_5H_9O_2N_2Br$ requires Br = 38·23%), and *bromomalonmonoisobutylamide*, m. p. 156° (Found : Br = 33·64. $C_7H_{13}O_2N_2Br$ requires Br = 33·72%), separate from alcohol–benzene in needles. *Bromomalonmonoethyl-*

mono-p-*bromophenylamide*, m. p. 179° [Found : Br (malonyl) = 22·08. $C_{11}H_{12}O_2N_2Br_2$ requires Br (malonyl) = 21·98%], *bromo-malonmono*iso*propylmono*-p-*tolylamide*, m. p. 179° (Found : Br = 25·31. $C_{13}H_{17}O_2N_2Br$ requires Br = 25·54%), and *bromomalon-monoisobutylmono*-p-*tolylamide*, m. p. 148° (Found : Br = 24·56. $C_{14}H_{19}O_2N_2Br$ requires Br = 24·44%), separate from dilute alcohol in needles. *Bromomalonmonoisopropylamide*, m. p. 192° (Found : Br = 35·60. $C_6H_{11}O_2N_2Br$ requires Br = 35·83%), *bromomalon-monoethylmonoisopropylamide*, m. p. 172° (Found : Br = 31·71. $C_8H_{15}O_2N_2Br$ requires Br = 31·84%), and *bromomalonmono*-p-*tolylamide*, m. p. 202° (Found : Br = 29·50. $C_{10}H_{11}O_2N_2Br$ requires Br = 29·48%), separate from ethyl acetate, benzene, or acetic acid–water in needles.

Bromomalon-p-*toluidide*.—The substance described (J., 1921, **119**, 359) as melting at 211° would not give a regular velocity coefficient, and proved to be a constant-crystallising mixture of the dibromo- and unchanged compounds.

Malon-*p*-toluidide (5 g.), dissolved in 300 c.c. of boiling acetic acid, was slowly treated with 10 c.c. of a 10% solution of bromine in the same solvent. Throughout the addition (20 minutes) the solution was vigorously shaken, and maintained at the boiling point. On cooling, the pure bromomalon-*p*-toluidide crystallised. It separated from acetic acid in plates, m. p. 217° (Found : Br = 22·00. $C_{17}H_{17}O_2N_2Br$ requires Br = 22·14%).

Velocity Measurements.

Methyl alcohol containing 4% of water and 2% of acetic acid (by volume) was an excellent solvent for the substances under investigation, concordant readings being obtained with the minimum of interference from side reactions. The methyl alcohol was treated with alkaline hypoiodite to remove acetone, dried, and distilled. The acetic acid was of the quality already described (J., 1921, **119**, 364). The quantity of potassium iodide used was that required by the equations :

a. . . . . $:CHBr + HI = :CH_2 + IBr$ (measured reaction)
b. . . . . $IBr + HI = I_2 + HBr$ (instantaneous reaction)

The calculations were therefore based on the expression $dx/dt = k'(a - x)(2a - 2x)$, which gives on integration, $k = 2k' = x/at(a - x)$. For convenience, the values of k are given in the tables and not those of k'.

Owing to the rapidity of some of the reactions, the experimental error is greater than is usual in such determinations.

Determination of the Velocity Coefficients.

Temp. 30·2°.

R'.	R''.	No. of deterns.	Limits of k.	Mean.	No. of deterns.	Limits of k.	Mean.	$k_{30\cdot2°}/k_{25°}$
NH_2	NH_2	7 *	0·79—0·82	0·81	6 *	1·11—1·15	1·14	1·41
NH_2	NHEt	6 *	0·91—0·93	0·93	6 *	1·41—1·45	1·43	1·54
NH_2	$NHPr^\beta$	6	0·92—0·97	0·95	7 *	1·44—1·51	1·47	1·55
NHMe	NHMe	8 *	0·98—1·04	1·01	7 *	1·59—1·69	1·64	1·62
NHEt	NHEt	8 *	1·07—1·15	1·12	6 *	1·78—1·87	1·83	1·63
NH_2	$NH\cdot C_4H_9$ (iso)	7	1·10—1·14	1·12				
NHEt	$NHPr^\beta$	4	1·41—1·44	1·42				
$NHPr^\beta$	$NHPr^\beta$	7 *	1·45—1·54	1·50	7 *	2·14—2·28	2·19	1·46
$NH\cdot C_4H_9$ (iso)	$NH\cdot C_4H_9$ (iso)	6 *	1·56—1·64	1·60	6 *	2·67—2·82	2·75	1·72
NH_2	$NH\cdot C_6H_4Me$ (p)	8 *	3·12—3·21	3·15	6 *	5·30—5·38	5·33	1·69
NHMe	,,	7	3·94—4·05	3·99	5 *	6·98—7·17	7·06	1·77
NHEt	,,	7	4·25—4·45	4·34	6 *	7·71—7·86	7·78	1·79
$NHPr^\beta$	,,	6	5·42—5·71	5·57	8	8·14—8·54	8·34	1·50
$NH\cdot C_4H_9$ (iso)	,,	7	5·81—6·04	5·91	8	8·43—9·11	8·77	1·49
$NH\cdot CH_2Ph$	,,	7	5·99—6·09	6·04	7	8·66—9·02	8·85	1·46
NH_2	$NH\cdot C_6\ddot{H}_4Br$ (p)	6	6·50—6·75	6·61	6 *	10·6—11·3	11·0	1·66
NHMe	,,	6	7·80—8·12	8·0				
NHEt		6	8·89—9·25	9·11				
OH	$NH\cdot C_6\ddot{H}_4Me$ (p)	3	9·2—10·2	9·6				
OEt	,,	6	13·0—13·7	13·3				
$NH\cdot C_6H_4Me$ (p)	,,	7	16·8—18·7	17·5	5	19·5—20·8	20·2	1·14

* In these experiments, initial concentration of bromo-compound = 0·008614 g.-mol./litre.
  In other ,, ,, ,, ,, ,, ,, = 0·004307 ,,

CVI.—The Velocity of Reaction in Mixed Solvents. Part VIII. The Velocity of Formation of certain Quaternary Ammonium Salts.

By HAMILTON McCOMBIE, HUGH MEDWYN ROBERTS, and HAROLD ARCHIBALD SCARBOROUGH.

In a previous communication (J., 1923, **123**, 1229), the velocity of formation of certain quaternary ammonium salts in mixed solvents was studied; and it was suggested that, if the curve showing the relation between k and the percentage composition of the solvent were divisible into linear sections, it would seem that not only had a solvent complex been formed, but also that this complex underwent further complex formation with one of the reactants or reaction products.

In order to obtain further information the velocity of formation of quaternary ammonium salts has been studied in different solvent pairs.

The Addition of Allyl Bromide to Pyridine in Benzene–Nitrobenzene Mixtures.

This reaction was studied by Hawkins (J., 1922, **121**, 1179); and it was shown that the existence of a complex between the solvent and a reactant was not to be expected. The velocity of formation of the quaternary ammonium salt was studied in nitro-benzene–benzene mixtures at 30°; the experimental results are shown in Tables I and II. The curve (Fig. 1) was found to be divisible into three linear sections which would intersect at the compositions 61·2 and 27·4% of nitrobenzene. Such compositions agree closely with those demanded by the complexes $C_6H_5 \cdot NO_2, C_6H_6$ and $4C_6H_6, C_6H_5 \cdot NO_2$, respectively.
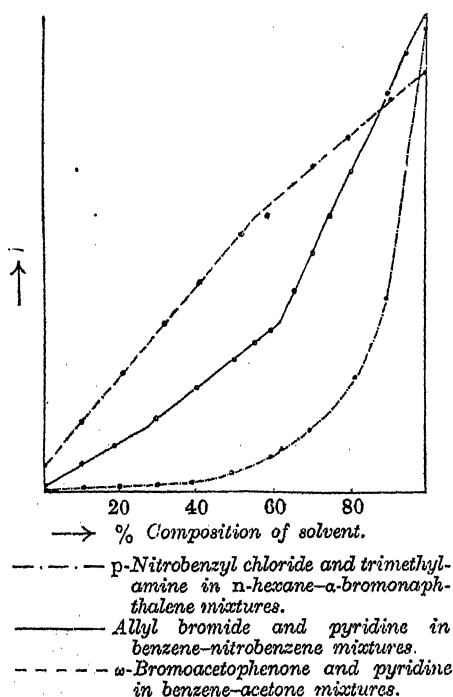
These results correspond with those obtained in the case of the reaction between trimethylamine and p-nitrobenzyl chloride (*loc. cit.*).

An examination of the physical constants for benzene–nitrobenzene mixtures showed that the only evidence of complex formation is the occurrence of a maximum in

FIG. 1.

$\longrightarrow$ % Composition of solvent.

— · — · — p-Nitrobenzyl chloride and trimethyl-amine in n-hexane–α-bromonaph-thalene mixtures.

———— Allyl bromide and pyridine in benzene–nitrobenzene mixtures.

— — — — ω-Bromoacetophenone and pyridine in benzene–acetone mixtures.

the viscosity curve at 62% of nitrobenzene (*Amer. J. Sci.*, 1896, [iv], **2**, 336).

The refractive index of benzene–nitrobenzene mixtures at 15° for the D line has been determined; the results are given in Table III. The curve is slightly bowed, but shows no marked change in direction.

A most noticeable point about this reaction was the form in which the quaternary ammonium salt was precipitated. In only one solvent composition—60% of nitrobenzene—did it appear to be a solid; in mixtures containing 55 and 65% of nitrobenzene the precipitate was semi-solid, and at all other compositions of the solvent it appeared as a dark red oil. That this change in the

appearance of the ammonium salt should occur at the point of inflection may have no significance, yet it does serve to illustrate our view that, although a curve may be divisible into linear sections, it does not follow that a sudden change occurs at the point of inflection; but rather that this change is occurring over a range of solvent composition. The point of inflection is the point at which the maximum effect is produced and any change in the direction of the curve must be supposed to originate at this point.

The Addition of ω-Bromoacetophenone to Pyridine in Benzene–Acetone Mixtures.

This reaction has been studied by Clarke (J., 1910, 97, 416) in alcoholic solution at 55·6°. The velocity of formation of the ammonium salt was measured in benzene–acetone mixtures at 30°; the experimental results are shown in Tables V and VI. The curve (Fig. 1) appears to be divisible into two linear sections which would intersect at 55% of acetone. Such a composition would agree with the complex $2C_3H_6O,C_6H_6$, which requires 54·6% of acetone. It is to be noted that the value of k in 60% acetone lies away from either section of the curve and thus tends to emphasise the fact that the curve consists of two linear sections. It is felt, however, that this coincidence must not be stressed, as the difference between the values of k in two consecutive solvent mixtures is only about three or four times the experimental error. The general shape of the curve is worthy of note. The reaction proceeds in pure acetone about 18 times as fast as in pure benzene; as the percentage of benzene in the solvent is increased, the value of k falls slowly but is always greater than the value of k calculated on the assumption that k will lie on a straight line joining the values in the pure solvents.

In all cases previously studied, the addition of that solvent in which the reaction proceeds more slowly causes a large decrease in the value of k. If in the case of the acetone–benzene mixtures a straight line be drawn joining the values of k in the two pure solvents, the maximum deviation of the curve from this straight line is equivalent to only about 20% in the value of k. In all other cases considered, this deviation would be equivalent to anything between 100 and 1000%.

The Addition of p-Nitrobenzyl Chloride to Trimethylamine in n-Hexane–α-Bromonaphthalene Mixtures.

The velocity of addition of p-nitrobenzyl chloride to trimethylamine has been measured by von Halban (Z. physikal. Chem., 1913, 84, 129) in solvents of widely differing chemical character.

It was found that, at 30°, the time for half the reaction to be completed in n-hexane was some 80 days and but some 4 hours in α-bromonaphthalene solution. The difference in reaction velocity is so great, in these two solvents, that it is comparable with the velocity of saponification of esters in alcohol–water mixtures. The use of such an inert solvent as n-hexane might be expected to exclude the possibility of complex formation between the solvents; thus the curve would represent a reaction proceeding in substances which play no *rôle* but that of solvent. The experimental results are shown in Tables VIII and IX; the curve (Fig. 1) is smooth and not divisible into linear sections.

A comparison of this reaction with the reaction studied in benzene–acetone mixtures shows the marked difference brought about by the addition of that solvent in which the reaction velocity is small. The first addition of n-hexane lowers the value of k to about 45% of the value of k in pure α-bromonaphthalene; for each additional 10% of n-hexane the constant is approximately halved. The maximum deviation of k from the value of k calculated on the assumption that a linear relationship holds is approximately 2200% and the deviation is negative.

EXPERIMENTAL.

The benzene and nitrobenzene were prepared and purified in the manner previously described; the n-hexane, α-bromonaphthalene, and acetone (B.D.H. products) were subjected to one fractional distillation. The densities of the benzene–acetone and the n-hexane–α-bromonaphthalene mixtures, recorded in Tables IV and VII respectively, were determined in the manner previously described (J., 1923, 123, 1229).

The pyridine (Kahlbaum) was fractionally distilled, the portion boiling at 116° being retained; the allyl bromide was similarly treated and the portion used boiled at 70·5°. The p-nitrobenzyl chloride (m. p. 71°) and the ω-bromoacetophenone (m. p. 51°) were prepared by the usual methods.

The solutions of the reactants were prepared by direct weighing, except in the case of the trimethylamine, the concentration of which was determined by titration. The velocity measurements were made at 30° $\pm$ 0·1°. The reactants were contained in sealed tubes; some 10 or 11 tubes were employed for each determination. The filling, draining, and sealing of the tubes were carried out with the tube partly immersed in ice-water. The zero time was taken as that moment at which the tube was placed in the thermostat. The progress of the reaction was followed by titrating the ionic halogen according to Volhard's method.

The velocity coefficient was calculated from either the equation :

$$k = 2 \cdot 302/(a - b)t \cdot \{\log (a - x)/(b - x) \cdot b/a\} \quad . \quad . \quad . \quad (1)$$

or

$$k = x/t\sqrt{ab(a - x)(b - x)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a and b are the initial concentrations in g.-mol. per litre and t is the time in minutes. Equation 2 was used in those cases in which a and b were nearly the same.

Representative results are shown in Tables II, VI, and IX.

The refractive indices recorded in Table III were determined at 15° with a Pulfrich refractometer.

TABLE I.

Nitrobenzene–Benzene Mixtures at 30°

Nitro-benzene %.	$c_{pyridine}$ (g.-mol./litre).	$c_{bromide}$ (g.-mol./litre).	Limit k.	
100	0·3504	0·3493	0·0147 —0·0151	0·0150
95	0·3503	0·3509	0·0138 —0·0145	0·0139
90·2	0·3504	0·3494	0·0122 —0·0128	0·0126
84·8	0·3531	0·3500	0·0108 —0·0112	0·0110
80	0·3500	0·3515	0·0102 —0·0105	0·0103
74·7	0·3510	0·3524	0·0085 —0·0089	0·0086
70	0·3517	0·3500	0·0069 —0·0071	0·00705
65·1	0·3520	0·3495	0·0061 —0·0064	0·00615
60	0·3515	0·3493	0·0049 —0·0053	0·00505
54·7	0·3525	0·3509	0·0044 —0·0046	0·00455
50·2	0·3501	0·3515	0·0039 —0·0042	0·00405
39·7	0·3526	0·3515	0·00305—0·00315	0·0031
29·9	0·3506	0·3510	0·00205—0·00220	0·00215
19·6	0·3500	0·3512	0·00132—0·00136	0·00135
10	0·3535	0·3520	0·00078—0·00081	0·00080
0	0·3507	0·3947	0·00032—0·00034	0·0003

TABLE II.

Nitrobenzene–Benzene Mixtures at 30°.

84·8% of Nitrobenzene.			19·6% of Nitrobenzene.		
$c_{amine} = 0 \cdot 3531.$ $c_{bromide} = 0 \cdot 3500$ (g.-mol./litre).			$c_{amine} = 0 \cdot 3500.$ $c_{bromide} = 0 \cdot 3512$ (g.-mol./litre).		
Time (mins.).	x.	k.	Time (mins.).	x.	k.
32	0·0381	0·0108	363	0·0528	0·00136
108	0·1012	0·0107	1046	0·1135	0·00132
146	0·1269	0·0110	1413	0·1391	0·00133
178	0·1440	0·0111	1780	0·1594	0·00134
207	0·1568	0·0110	2468	0·1886	0·00135
236	0·1680	0·0110	2921	0·2036	0·00136
262	0·1764	0·0110	3209	0·2120	0·00136
319	0·1960	0·0112	3914	0·2255	0·00134
347	0·2017	0·0110	4355	0·2350	0·00134

TABLE III.

Refractive Indices of Benzene–Nitrobenzene Mixtures at 15°.

Nitrobenzene %	100	95	90·2	84·85	81·1	74·75
$n_D^{15°}$	1·55415	1·55130	1·54767	1·54351	1·54150	1·53791
Nitrobenzene %	69·6	65·15	62·13	59·05	54·7	39·7
$n_D^{15°}$	1·53493	1·53262	1·53104	1·52948	1·52734	1·52028
Nitrobenzene %	28·85	19·65	10	0		
$n_D^{15°}$	1·51588	1·51171	1·50785	1·50403		

TABLE IV.

Density of Acetone–Benzene Mixtures at 15°.

Acetone %	100	89·95	80·16	69·47	60·29	49·69
$d_{4°}^{15°}$	0·79769	0·805607	0·81370	0·82272	0·83020	0·83938
Acetone %	40·29	29·72	20·09	9·94	0	
$d_{4°}^{15°}$	0·84768	0·85680	0·86556	0·87490	0·88453	

TABLE V.

Benzene–Acetone Mixtures at 30°.

Acetone %.	$c_{pyridine}$ (g.-mol./ litre).	$c_{bromoacetophenone}$ (g.-mol./ litre).	Limit k.	k.
100	0·0498	0·0508	0·0860—0·0880	0·0875
90·65	0·0499	0·0504	0·083 —0·084	0·0835
79·85	0·0691	0·0666	0·073 —0·076	0·0755
70	0·0691	0·0666	0·067 —0·070	0·069
59·95	0·0686	0·0663	0·0585—0·0605	0·0595
49·5	0·0679	0·0662	0·0535—0·055	0·054
40	0·0681	0·0661	0·042 —0·047	0·044
29·25	0·0673	0·0664	0·033 —0·0365	0·034
20·10	0·0681	0·0663	0·0245—0·026	0·025
10	0·0685	0·0678	0·014 —0·015	0·0145
0	0·0683	0·0661	0·0046—0·005	0·0048

TABLE VI.

Benzene–Acetone Mixtures at 30°.

79·85% of Acetone.			20·10% of Acetone.		
$c_{pyridine} = 0·0671$. $c_{bromoacetophenone}$ 0·0656 (g.-mol./litre).			$c_{pyridine} = 0·0681$. $c_{bromoacetophenone} =$ 0·0663 (g.-mol./litre).		
Time (mins.).		k.	Time (mins.).	x.	k.
76	0·0183	0·0758	253	0·0203	0·0252
176	0·0312	0·0755	430	0·0286	0·0256
204	0·0337	0·0760	901	0·0406	0·0253
244	0·0366	0·0759	1021	0·0426	0·0255
283	0·0389	0·0754	1112	0·0442	0·0258
318	0·0407	0·0752	1250	0·0456	0·0252
338	0·0416	0·0756	1297	0·0461	0·0251
371	0·0431	0·0753	1407	0·0469	0·0244
412	0·0443	0·0735			

TABLE VII.

α-Bromonaphthalene–n-Hexane Mixtures at 15°.

α-$C_{10}H_7$Br %	100	90	79·9	70	59·9	49·75
$d_{4°}^{15°}$	1·47682	1·33641	1·21802	1·11572	1·02959	0·95566
α-$C_{10}H_7$Br %	40·1	29·85	19·95	10·1	0	
$d_{15°}^{15°}$	0·89003	0·83120	0·78155	0·73521	0·69411	

TABLE VIII.

α-Bromonaphthalene–n-Hexane Mixtures at 30°

$C_{10}H_7$Br %.	c_{amine} (g.-mol./ litre).	$c_{chloride}$ (g.-mol./ litre).	Limit k.		k.
100	0·1778	0·1068	0·0172	—0·0177	0·0175
90	0·1583	0·1075	0·0073	—0·0079	0·0075
79·9	0·1769	0·0997	0·0033	—0·0038	0·0036
70	0·1272	0·1010	0·00195	—0·00205	0·00203
59·9	0·2073	0·0666	0·00120	—0·00126	0·00123
49·75	0·1345	0·0703	0·00071	—0·00073	0·00072
40·1	0·1285	0·0458	0·00036	—0·00042	0·00040
29·85	0·1302	0·0454	0·00022	—0·000245	0·00023
19·95	0·1251	0·0386	0·000135	—0·00016	0·00015
10·1	0·1373	0·0485	0·000097	—0·00011	0·000105
0	0·1262	0·0403	0·000076	—0·000080	0·000078

TABLE IX.

α-Bromonaphthalene–n-Hexane Mixtures at 30°.

100% of α-Bromonaphthalene.

$c_{amine} = 0·1778.$ $c_{chloride} = 0·1068.$
(g.-mol./litre).

29·85% of α-Bromonaphthalene.

$c_{amine} = 0·1302.$ $c_{chloride} = 0·0454.$
(g.-mol./litre).

Time (mins.).		k.	Time (mins.).		k.
92	0·0245	0·0172	4,320	0·0055	0·000234
154	0·0354	0·0172	8,835	0·0092	0·000223
193	0·0436	0·0177	12,983	0·0137	0·000224
232	0·0491	0·0177	18,730	0·0191	0·000227
276	0·0541	0·0175	34,758	0·0315	0·000224
349	0·0614	0·0175	60,466	0·0365	0·000245
384	0·0651	0·0177	51,775	0·0344	0·000244
404	0·0655	0·0172	79,090	0·0384	0·000221

CVII.—*A New Method of Flame Analysis.*

By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and HENRY
ROBINSON.

IN the course of an investigation of the phenomena immediately
attendant on the ignition of an inflammable gaseous mixture, the
authors have been under the necessity of obtaining instantaneous
photographs of the flame-front at very small and accurately known
intervals of time after ignition. The revolving-film method of
photography, first used by Mallard and Le Chatelier (*Ann. Mines,*
1883, [viii], 4, 312) for studying the propagation of flame in tubes,
normally yields only a time–distance curve with respect to the flame
as a whole; it cannot register, for example, the shape of the flame-
front at any given stage in the propagation. Mason and Wheeler's
modification of the method (J., 1920, **117**, 1233) enabled them to
obtain satisfactory photographs of the flame-front during the
" uniform movement," but was not applicable if the speed of the
flame was irregular.

The apparatus to be described has been successfully used to
obtain such photographs as were desired, namely, snapshots of
flames at any interval of time after their initiation. When the
flame is moving (along a tube, for example) a number of snapshots
showing consecutive phases of the propagation can be photographed
on one plate. This method of flame analysis has given such satis-
factory results that the authors have been asked to describe their
apparatus in detail, in the belief that it will prove of value to other
workers.

The most important element of the apparatus is a revolving
shutter, D, Fig. 1, consisting of a steel disk, two metres in circum-
ference, from the periphery of which have been cut 24 windows,
each 3 cm. square and spaced at intervals of 15°. This disk is
rotated at any desired speed in front of the lens of a camera with
a stationary photographic plate, in such a manner that the windows
periodically allow light to pass to the lens. According to the
character of the flame to be photographed, a few or one only of the
windows may be required; the remainder can readily be closed by
pasting paper over them. The measurements of the times of the
exposures and their synchronisation with the movements of the
flame are effected by electrical means.

The operation of the several electric circuits is brought about
by means of a radial knife, K, held in a light carrier fixed near
the periphery of the disk. Normally the knife projects about a
centimetre beyond the carrier, but it can be withdrawn, against

Fig. 1.

PLAN.
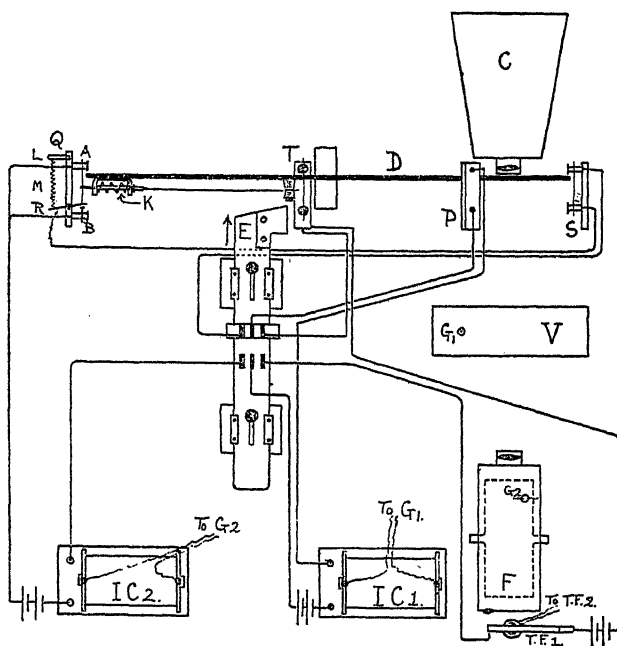
ELEVATION.
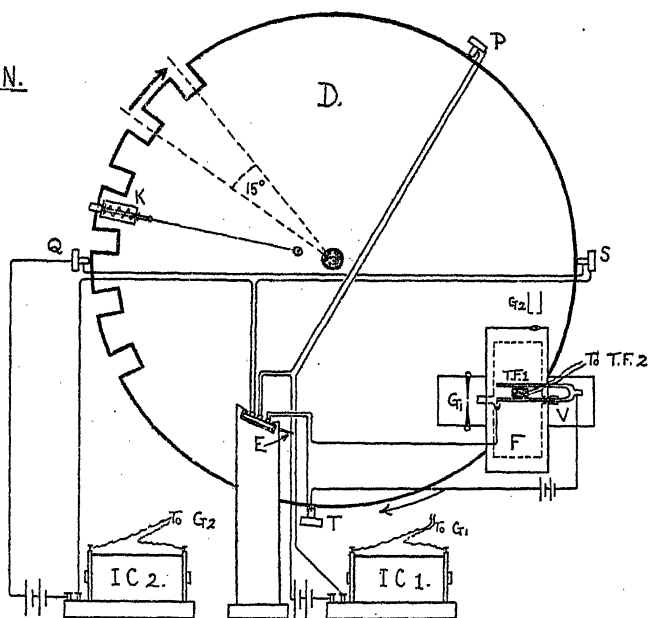
the compression of a light spring, by a thread of cotton which, when taut, is clamped in a terminal near the axle of the disk. This retaining thread can be cut when desired by moving the cutter, E, towards the face of the disk. The act of moving the cutter towards the disk also automatically closes all the three electric circuits that are used.

Astride the edge of the disk, and parallel to its axis, are four stirrups, P, S, T, and Q. The first three of these are identical in form, each consisting of two terminals, 6 cm. apart, mounted on ebonite rod, with flexible leads soldered to the legs of the terminals, the heads being bridged by 5-ampere fuse wire. The fourth stirrup, Q, is of somewhat different design. It consists of a piece of copper strip, R, loosely pinned to an ebonite rod, which carries two terminals, A and B, in the position indicated in plan in Fig. 1. One end of the strip is connected by the spring, M, to a peg, L, so that normally it is drawn by the tension of the spring into contact with the terminal, B. Contact can be prevented by loop-ing a piece of fuse wire round the other end of the strip and clamping the taut wire in the terminal A. Assuming the electrical connexions to be made as indicated in the diagram, current will flow through terminal A, the fuse wire, and the copper strip. If the fuse wire is ruptured, the current is momentarily interrupted by just so long as it takes the spring to draw the released strip into contact with terminal B, so re-establishing the circuit.

The position of each stirrup is adjusted so that its fuse wire lies as close to the edge of the disk as possible. The three stirrups, Q, S, and T, are placed in permanent positions, since their respective functions are constant. Q and S are placed in the positions indicated in Fig. 1, 180° apart, S being fixed so that the radial knife, K, is just in contact with the fuse wire when the first window in the disk is exactly opposite the lens of the camera; the position of T is such that the radial knife has just passed it when the retain-ing thread engages with the cutter, E. The stirrup P, the function of which relates to the ignition of the inflammable mixture, is the only one without a fixed position. As is explained later, its position is determined by the interval desired between the ignition and the first exposure of the photographic plate.

The revolving film camera, F, besides serving as a chronograph, records the speed of propagation of the flame. The roof of the box enclosing this camera carries a small lens which focusses on the film a short spark gap, G 2. In a similar way the flashes from an electrically-controlled mercury-break tuning-fork, TF 1, at the back of the box are registered on the film by another lens and record a time-scale. The electromagnet of the tuning-fork TF 1 is con-

nected in series with the circuit of a second tuning-fork, TF 2, of the same frequency, vibrating in unison with it, although no flashes appear at the mercury-break of the first fork until the electric circuit of which it forms a part has been completed.

Each of the three electric circuits involved in the apparatus has its own sliding switch on the cradle of the cutter, E. The igniting-circuit for the inflammable mixture comprises a battery in series with a cradle switch, the stirrup P, and the primary of the induction coil, IC 1. The second circuit contains a battery in series with stirrups Q and S, a cradle switch, and the primary of an induction-coil, IC 2. The secondary windings of the coils IC 1 and IC 2 are connected to the spark gaps, G 1 and G 2, respectively, the tremblers of both coils being locked. The third circuit contains a battery in series with stirrup T, a cradle switch, and the mercury-break of the tuning fork, TF 1.

The function of the various circuits will probably be best understood from a description of an experiment. It will be assumed that the radial knife has been withdrawn within the periphery of the disk by its retaining thread, that the cutter is drawn back so that the cradle switches are open, and that the four stirrups are fitted with fuse wire in the manner already described. Only the first six windows in the disk are open. The disk and the revolving drum of the film camera, F, have reached their full speed, the explosion-vessel, V, to be photographed is filled with the required mixture, and the tuning forks are vibrating steadily.

On driving the cutter E sharply forward towards the disk, all three electric circuits are automatically closed, so that the current flows through the primary windings of the two coils and across the mercury-break of the tuning fork, TF 1; the flashes from this mercury-break are registered on the revolving film of the camera F.

The retaining thread of the radial knife having been severed on coming in contact with the razor edge of the cutter, the knife moves outward to its natural position beyond the periphery of the disk, and severs all four fuse-wires in turn.

The rupture, at stirrup Q, of the primary circuit of the coil IC 1 causes a spark to pass across the gap G 2, registering on the revolving film the instant at which one half-revolution of the disk is begun, but, owing to the special form of this stirrup, the electric current is re-established after an instant's delay. Similarly, the rupture of the fuse-wire of stirrup P causes a spark across the gap G 1. This spark ignites the mixture in V and its passage is registered on the revolving film. When the knife, after passing stirrup Q, has moved through 180° (equivalent to 12 windows in the disk), it encounters the fuse-wire of stirrup S, whilst, at the same instant,

the first window in the disk appears opposite the lens of the plate camera, C. The spark which passes across the gap G 2 when the radial knife severs the fuse wire of stirrup S registers on the revolving film the instant at which the first exposure is made, and this coincides with the completion of one half-revolution of the disk. Finally, as the knife severs the wire of stirrup T, the tuning-fork flashes cease.

The film record of the various sparks and of the time-scale supplies all the information necessary to calculate the interval between the time of ignition of the inflammable mixture and the first exposure of the plate, and intervals between successive exposures.

CVIII.—*The Movement of Flame in Closed Vessels.*

By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER.

WHEN considering the inflammation of mixtures of methane and air in closed spherical vessels (Wheeler, J., 1918, **113**, 840), it was assumed that, if the ignition of the mixture is exactly at the centre of a sphere, the propagation of flame follows regular concentric spherical surfaces in such a manner that the boundary is reached simultaneously at all points. For, except with very slowly moving flames, or, possibly, in very large vessels, convection currents would not appreciably affect the speed in any particular direction. It was shown experimentally that, with any mixture of methane and air containing more than 7·5 and less than 12·5% of methane, the time taken for flame to travel from the centre of a closed vessel to the top and to the bottom was the same.* Further, it could be deduced from the times taken for the development of the maximum pressures when a series of mixtures of methane and air was inflamed in spheres of 9·75 cm. and 15·6 cm. radius, that (ignoring the initial impetus given by the impulsive discharge used to cause ignition) the speed

* With mixtures containing less than 7·5 and more than 12·5% of methane, in which the rate of propagation of flame is slow, flame reached the bottom of the vessel later than it reached the top by an interval that varied with the methane-content of the mixture.

PLATE I.
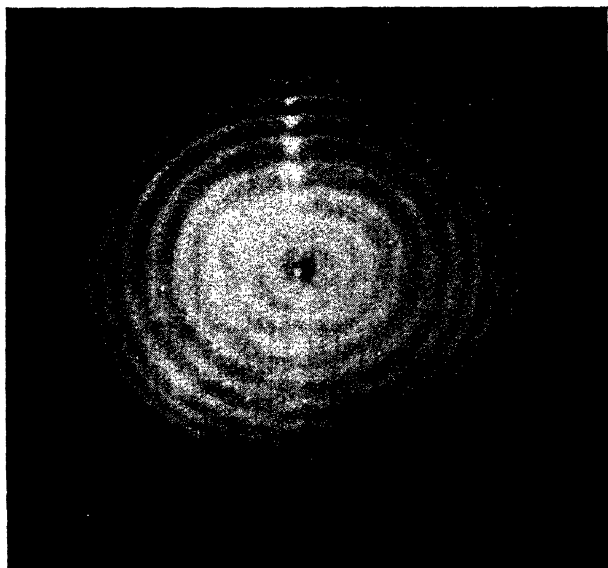
Fig. 1.—*Central ignition.*
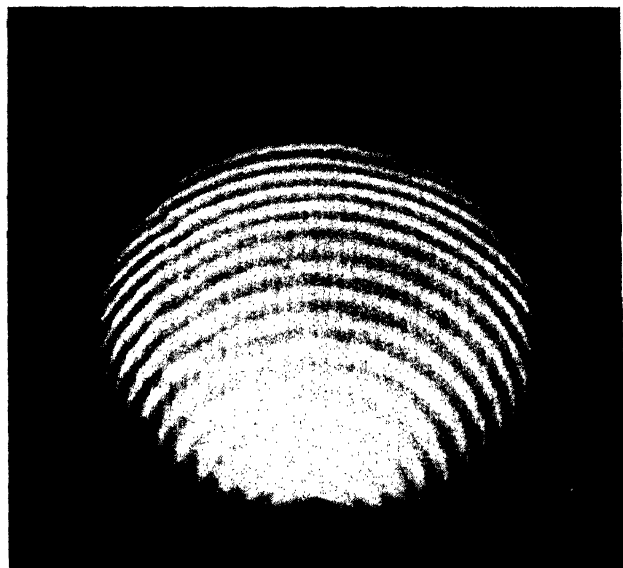
Fig. 2.—*Ignition at bottom.*

Propagation of flame within a closed sphere. Successive intervals of 4·58 milliseconds.

PLATE II.
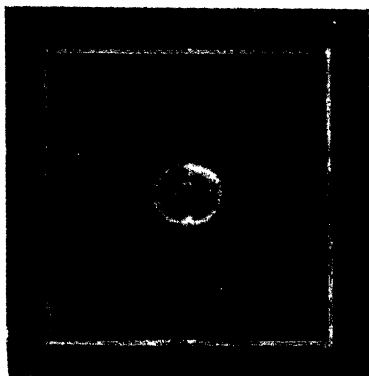
FIG. 1.—*After* 9·16 *milliseconds.*
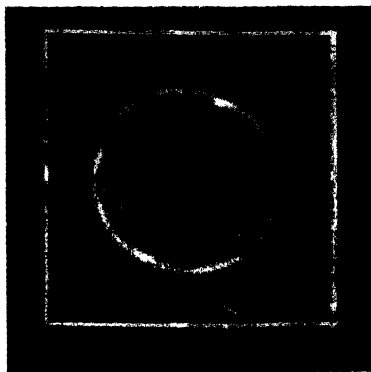
FIG. 2.—*After* 22·9 *milliseconds.*
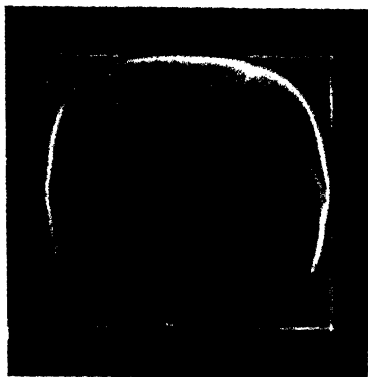
FIG. 3.—*After* 36·44 *milliseconds. Flame just touching sides of cylinder.*

FIG. 4.—*After* 36·64 *milliseconds and subsequently at intervals of* 4·58 *milliseconds.*

Propagation of flame within a closed cylinder.   Central ignition.

at which flame travelled from the centre to the walls of the spheres was uniform (*loc. cit.*, p. 852),

We have recently been able to obtain experimental proof of the correctness of these assumptions regarding the manner in which flame spreads from the centre of a closed spherical vessel, by means of the apparatus described elsewhere in this journal (Ellis and Robinson, preceding paper).

Fig. 1, Plate I, is a reproduction of a series of photographs, taken at intervals of 4·58 milliseconds on the same stationary plate, of flame moving in a vertical plane away from the centre of a sphere of glass, 9 cm. in diameter. The duration of exposure of each photograph was 1·69 milliseconds. It will be seen that the flame " follows regular concentric spherical surfaces " and reaches the boundary simultaneously at all points; whilst, so soon as the initial impetus due to the secondary discharge used to ignite the mixture has died away, the speed of the flame becomes uniform. A companion series of photographs of the flame moving in a horizontal plane was identical.

Mallard and le Chatelier (*Ann. Mines*, 1883, [viii], **4**, 379), in connexion with their work on the pressures produced by gaseous explosions, made assumptions (from their time–pressure curves) regarding the movement of flame in a closed cylinder which we can now show to be correct. They used a cylinder the length and diameter of which were equal (17 cm.), and ignited the mixture at the centre. Their description of the manner in which the flame spread from the spark-gap can be freely translated as follows :

" Owing to the unfortunately faulty shape of our explosion-vessel, the propagation of flame assumed two phases. The inflammation, produced at the centre of the cylinder by the spark, is at first propagated away from the point of ignition as a kind of spherical wave which continuously increases in size until it touches the walls of the cylinder. The height of the cylinder being equal to its diameter, the wave (if it remains spherical) touches the sides and the top and bottom plates simultaneously. The second phase in the propagation then begins and continues until the flame reaches the curve of intersection of the end plates with the cylindrical walls.

" During the first phase, the propagation takes place without appreciable cooling, since the wave of flame has not yet touched the walls and there is therefore no loss of heat other than that arising from radiation and the small amount due to the abstraction, from the unburnt mixture in contact with the walls of the vessel, of the heat of compression caused by the expansion of the burnt mixture near the centre. Both these causes of loss can be regarded as negligible.

" During the second phase, on the contrary, cooling by the walls

takes place and increases as the propagation proceeds, since the area of the surface of the cylinder in contact with the flame increases."

The correctness of Mallard and le Chatelier's deductions can be judged from the photographs on Plate II, which show separate stages in the propagation of flame, in a vertical plane, from the centre of a glass cylinder 10 cm. long and 10 cm. in diameter. As with the photographs reproduced on Plate I, the interval between exposures was 4·58 milliseconds. The first photograph was taken 2 intervals after ignition, the second 3 intervals later, and the third, when the " spherical wave " has just touched the boundary of the vessel, after a further 3 intervals. The fourth photograph is

FIG. 1.

TIME IN SECONDS. (TIME 0 = TIME OF IGNITION).
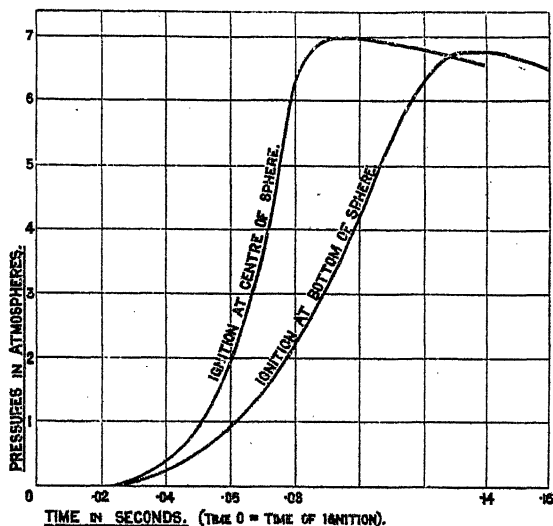
a composite one, showing successive stages, 8, 9, 10, and 11 intervals after ignition, which represent the second phase of the propagation, when the flame is squeezing itself into the " corners " of the cylinder. The boundary of the vessel is shown in each instance by white lines drawn on the photograph. It will be noticed that the centre of the vessel is re-illuminated after the flame has reached the sides. This phenomenon will be discussed in a later communication.

The extent to which cooling of the flame by the walls of a spherical vessel can occur when ignition is not central is illustrated in Fig. 2, Plate I. Ignition was at a spark-gap between electrodes which just passed through the walls of the sphere at the bottom, and the photographs were taken, in a vertical plane, at intervals of 4·58 milliseconds. The inflammable mixture had the same composition as in

the experiment illustrated in Fig. 1, and the intensity of the source of ignition was approximately the same.

It will be understood that cooling by the walls of the vessel, and consequent retardation of the flame, can affect not only the maximum pressure that a given mixture can produce when it is inflamed, but also the rate of development of pressure; so that when attempting to interpret the character of time–pressure curves obtained from gaseous explosions in closed vessels due consideration must be paid to the shape of the vessels and to the position of the point of ignition. The curves in the text (Fig. 1) illustrate this. Both were obtained by the inflammation of mixtures of methane and air of the same composition (10·15% of methane) in a spherical explosion-vessel of 4 litres capacity, similar in design to that described in J., 1918, **113**, 854. In one experiment, ignition of the mixture was at the centre of the sphere; in the other it was at the bottom. In the latter, the rate of development of pressure is considerably retarded and the maximum pressure attained is less.

Our thanks are due to the Explosives in Mines Research Committee and to the Safety in Mines Research Board for permission to publish this paper, which should be regarded as preliminary to a detailed study of the movement of flame in closed vessels.

SAFETY IN MINES RESEARCH BOARD LABORATORIES,
SHEFFIELD.   [*Received, January 28th*, 1925.]

NOTES.

3-*Chlorobenzopyrylium Derivatives*. By LESLIE RANDAL RIDGWAY and ROBERT ROBINSON.

WE have recently shown (J., 1924, **125**, 214) that the condensation of 2-hydroxy-3-ethoxybenzaldehyde and acetophenone or ω-bromoacetophenone under the influence of hydrogen chloride leads to 8-ethoxy-2-phenylbenzopyrylium chloride. Reduction does not occur, however, when ω-chloroacetophenone and ω-chloroacetylanisole are condensed in a similar manner with 2-hydroxy-3-ethoxybenzaldehyde. Characteristic pyrylium salts bearing a chlorine atom as a substituent in position 3 are so obtained.

3-*Chloro-8-ethoxy-2-phenylbenzopyrylium Ferrichloride*,
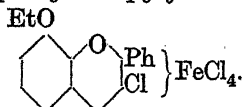
—A *ferrichloride* was precipitated by addition of concentrated

hydroferrichloric acid to a mixture of ω-chloroacetophenone (2 g.), 2-hydroxy-3-ethoxybenzaldehyde (2 g.), and glacial acetic acid (10 c.c.) which had been saturated with hydrogen chloride during 5 hours. The derivative was washed with ether and thrice crystallised from acetic acid (Found : C = 42·5 ; H = 3·2. $C_{17}H_{14}O_2Cl_5Fe$ requires C = 42·2; H = 2·9%), 1·0 g. of maroon prisms, m. p. 155°, soluble in alcohol to a yellow and in chloroform to an orange solution, was obtained. In a similar manner, but in doubled yield, ω-chloroacetylanisole gave 3-*chloro*-4'-*methoxy*-8-*ethoxy*-2-*phenyl-benzopyrylium ferrichloride*, which crystallises from acetic acid in highly lustrous, long, rectangular, brick-red plates, m. p. 150° (Found : C = 42·1; H = 3·3; Cl = 34·9. $C_{18}H_{16}O_3Cl_5Fe$ requires C = 42·1; H = 3·1; Cl = 34·6%). Each of these ferrichlorides readily yields a colourless pseudo-base from which the yellow oxonium salt can be regenerated by the action of mineral acids.—THE UNIVERSITY, MANCHESTER. [*Received, January 31st,* 1925.]

A Qualitative Test for Weak Bases. By ROBERT ROBINSON.

A SOLUTION of hydroferrichloric acid made by saturating concentrated hydrochloric acid with ordinary crystallised ferric chloride is added to a solution of the substance to be tested in light petroleum (b. p. 40—60°). Three layers are often produced : the lowest is an aqueous solution of ferric chloride and hydrochloric acid much more dilute than the reagent; the green or brown middle layer contains the weak base, ferric chloride, and hydrogen chloride; the top layer consists chiefly of light petroleum. This behaviour is clearly due to the formation of ferrichlorides and is exhibited by the majority of carbon compounds, containing oxygen, nitrogen or sulphur, that are sufficiently readily soluble in light petroleum. Positive results are obtained with all simple alcohols except methyl and ethyl alcohols (which are too soluble in water), *e.g.*, *iso*amyl alcohol, benzyl alcohol, *cyclo*hexanol; with aliphatic ethers, *e.g.*, diethyl ether, di*iso*amyl ether; with esters, *e.g.*, ethyl acetate, ethyl benzoate; with ketones, *e.g.*, *cyclo*hexanone, acetophenone; with aldehydes, *e.g.*, *n*-heptaldehyde, benzaldehyde; with phenol ethers, *e.g.*, anisole, veratrole; with nitro-compounds, *e.g.*, nitromethane, nitrobenzene; with nitriles, *e.g.*, acetonitrile, phenylacetonitrile; with thio-ethers, *e.g.*, diethyl sulphide; and with many other classes of compounds. More than two hundred cases have been tried and the following exceptions noted : carboxylic acids, acid chlorides (but not anhydrides, amides, or ester chlorides,

e.g., ethyl chloroformate gives positive results), thiophen, safrole, diphenyl ether. It is remarkable that the methylenedioxy-group should not confer oxonium character, but the other exceptions are easily understood, and diphenyl ether may be compared in this respect with diphenylamine.

Naturally, since water is present in the system, there is a certain minimum strength of a base below which this test is not diagnostic. Some practical applications may be indicated. (1) Traces of oxygenated and nitrogenous compounds may be removed from hydrocarbons by washing with hydroferrichloric acid. (2) Camphor oil contains safrole and camphor, and when a mixture of these substances is dissolved in light petroleum and hydroferrichloric acid is added, a green middle layer can be separated which gives solid camphor on treatment with water. Safrole remains in the light petroleum solution.—THE UNIVERSITY, MANCHESTER. [*Received, January* 31*st*, 1925.]

A New Portable Apparatus for the Analysis of Illuminating and Other Gases. By HUMPHREY DESMOND MURRAY.

THIS apparatus differs from previous modifications in that only one pipette is employed, and each absorbent is sucked up into the latter as required. The usual gas burette, C, is attached above to a three-way tap, one conduit of which leads to the external gas connexion, the other to the intermediate container, B, through a second three-way tap. The other conduit of the container is attached to the gas pipette, A, which has two alternative leads, so that the gas may be injected through the jet, D, and withdrawn through the upper tube. The container B is provided with a mercury reservoir attached to its lower end by a piece of flexible
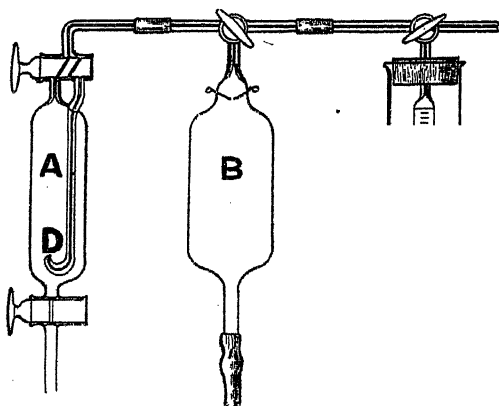
tubing. Before use, B is filled with mercury and C with some containing liquid, which in most cases may be slightly acidified water. If the absorbent does not act rapidly upon rubber tubing, the lower lead-in tube of A is attached thereby to the vessel containing the absorbent. If the use of rubber is not permissible, the lead-in tube of A is immersed directly in the absorbent, which is drawn into the pipette by lowering the mercury in B. The gas is then passed through the absorbent in a fine stream of bubbles and returned to the burette, where its contraction is measured. For the analysis of gaseous mixtures containing such gases as hydrogen and methane, a measured volume of air or oxygen is added to the gas in C, and the mixture passed into B, exploded, and returned to C, where any alteration in volume may be measured. Any products of the explosion can be measured as above described by absorption with suitable reagents in A. In the case of absorptions requiring the use of two absorbents, the second may be drawn into B. If, when bromine water is to be used, a layer of caustic potash is introduced above the mercury in B, the gas after treatment in the pipette may be passed first into B, where the bromine fumes are removed, and then into the burette. The apparatus permits of clean and rapid analyses, and since it is never permanently charged with reagent it is very portable.—IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON. [*Received, February 2nd,* 1925.]

CIX.—*The Relationship of Thyroxin to Tryptophan.*

By C. STANTON HICKS.

THYROXIN, the crystalline compound obtained from the thyroid gland by hydrolysis (Kendall, *J. Biol. Chem.*, 1919, **39**, 125; **40**, 265) has not been studied by any other observer with a view to corroborate or otherwise the evidence for its highly interesting structural formula as put forward by Kendall (*ibid.*, 1919, **40**, 268).

$$\text{(structural formula of thyroxin)}$$
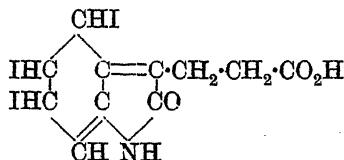
As was appreciated at the time, and pointed out by Barger (*Ann. Reports*, 1919, **16**, 160), the presence or absence of two additional hydrogen atoms in the benzene nucleus of the molecule as figured by Kendall would make only the small difference of 0·35% in the total hydrogen content, and such a substance, containing as it does some 67% of iodine and only 1·60% of hydrogen, offers difficulties to exact analysis. The substance also contains three asymmetric carbon atoms; this was unappreciated in the original paper (*loc. cit.*, p. 308).

In connexion with work on the etiology of goitre, it was considered that, assuming Kendall's formula to be correct, or substantially so, a likely starting point for the synthesis of thyroxin in the animal body would be tryptophan. In his original paper, Hopkins had suggested that tryptophan, the metabolism of which in the organism is as yet unknown, and which is of such vital importance for the life and growth of the animal, might be used in the manufacture of some internal secretion (*J. Physiol.*, 1901–2, **27**, 418; also 1912, **44**, 425). He further was able to show that tryptophan was not synthesised in the animal body.

Two methods were adopted in the initial investigation into the relationships of thyroxin and tryptophan. Rats were placed on diets containing known deficiencies of tryptophan, with the intention of following (*a*) basal metabolism changes, and (*b*) pathological changes in the thyroid and suprarenal glands, and a study of the ultra-violet absorption spectra of the two compounds was made. The former work, which is not yet complete, will be reported elsewhere. This paper is a preliminary one only, on the absorption spectrum relationships.

Apparatus.—A Hilger spectrometer for the ultra-violet, with a

rotating sector photometer, was first calibrated against a pure cadmium emission spectrum, using the high-tension condenser electric discharge, with cadmium electrodes. Subsequent absorption measurements were made using nickel electrodes, which give a spectrum rich in lines, beyond 2100 Å.U. A Sartorius micro-balance accurate to 0·00001 g. was used in making up the solutions for measurement.

Method.—Thyroxin "crystals" were obtained from Messrs. Squibb and Son of New York, and, in all, 20 mg. of the substance were used. The thyroxin was recrystallised by slowly passing carbon dioxide into its solution in N-sodium hydroxide (4 equivs., calculated from the formula). Thyroxin dissolves with great difficulty, and requires a high local concentration of alkali; in no case did the substance dissolve in its equivalent of sodium hydroxide as stated by Kendall and Osterberg (*J. Biol. Chem.*, 1919, 40, 268). This may have been due to the thyroxin (Squibb) not being pure enough, for on account of losses in dealing with small amounts of material, and the high cost of the substance, solubility experiments were not attempted on the crystals isolated in this work.

The thyroxin was separated from the solution in a centrifuge, washed by centrifuging with water, and dried in a vacuum desiccator. The melting point, determined under the microscope by comparison with that of phenolphthalein, was about 250° as nearly as could be estimated, as browning and decomposition began near this point. Under the microscope, the sheaves of needles depicted in the original paper were observed.

The absorption spectra were best obtained with aqueous alkaline solutions, prepared by suitably diluting a solution of thyroxin in alkali (4 equivs.). Using a 10 millimetre cell, and a comparison solution of alkali of equal concentration, a series of 18 photographs was taken at each of the following dilutions: $M/8,000$, $M/12,000$, $M/16,000$, $M/20,000$, $M/30,000$, $M/40,000$. The handling of such small amounts of material was the chief source of difficulty, and measurements were made in duplicate where possible.

According to Kendall, the enolic form will be present in the alkaline solution (*loc. cit.*).

Tryptophan was prepared by Onslow's modification (*J. Physiol*, 29, 451) of Hopkins and Cole's method (*ibid.*, 1901—2, 27, 418). The product was extracted by butyl alcohol in a vacuum after Dakin (*Biochem. J.*, 1917—18, 12, 290; *J. Biol. Chem.*, 1920—21, 44, 499), decolorised with animal charcoal, and recrystallised from 65% alcohol; m. p. 289°.

Measurements were made in alcoholic solution at concentrations of $M/10,000$, $M/30,000$, $M/40,000$, $M/50,000$.

2-Hydroxyindole-3-propionic acid was recrystallised from water and its absorption spectra were measured in concentrations of $M/10,000$, $M/20,000$, $M/30,000$, $M/40,000$, and $M/50,000$.

In order to compare the effect of substitution of iodine in the molecule on the absorption curve of tryptophan with that due to the iodine in thyroxin, attempts were made to prepare iodotryptophan,

Thyroxin — o — o —   Tryptophan — × — × —
2-Hydroxyindole-3-propionic acid — ▲ — ▲ —
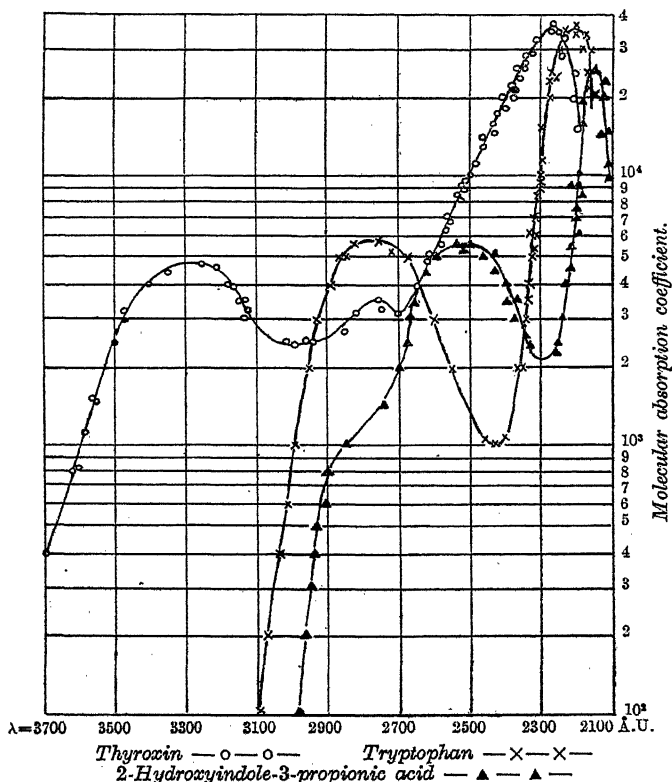
Molecular absorption coefficient = $1/d$. ($\log I_0 - \log I)/c$; *where* I_0 = *intensity of incident light ;* I = *intensity of transmitted light ;* d = *thickness of absorbing layer in cm. ; and* c = *molecular concentration.*

but the resulting compound has not so far been obtained with a constant composition (compare Neuberg, *Biochem. Z.*, 1907, **6**, 276, and Koch, *J. Biol. Chem.*, 1913, **14**, 106).

Monoiodoisatin was therefore prepared by treating a saturated solution of isatin (m. p. 201°) in glacial acetic acid with iodine monochloride, more than three times the theoretical amount being necessary (compare Borsche and others, *Ber.*, 1924, **57**, [*B*], 1770; Michael and Norton, *Ber.*, 1878, **11**, 107). The compound separate 1

E E ?

in brilliant, glistening, scarlet, crystalline powder form, m. p.
264·5—265·5°, and was very sparingly soluble in alcohol or glacial
acetic acid (Found : I = 46·05, 46·31.   Calc., I = 46·12%).

A large series of dilutions was used, from $M/3000$ to $M/30,000$
by steps of $M/3000$, in order to ensure that no small variations in
the curve were overlooked.

=5700 5500 5300 5100 4900 4700 4500 4300 4100 3900 3700 3500 3300 3100 2900 2700 2500 2300 2100 Å.U.

Isatin — ▲ — ▲ —   *Monoiodoisatin* — o — o —
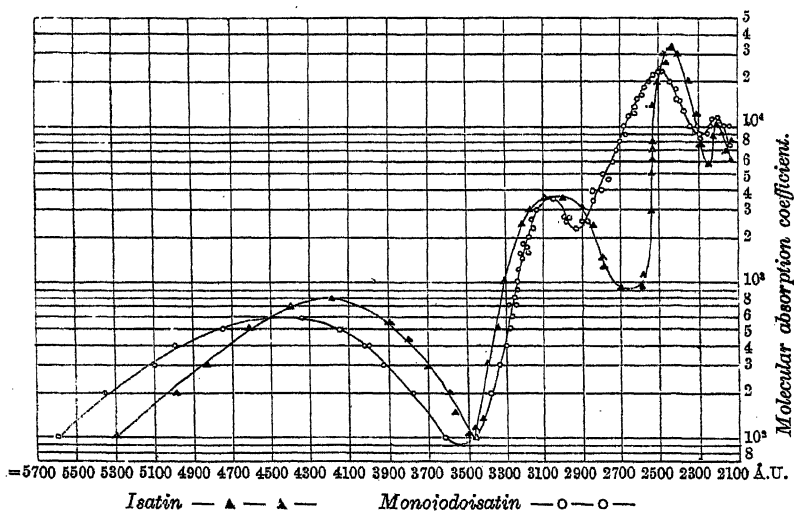
Discussion.

Examination of the ultra-violet absorption spectra of thyroxin,
tryptophan, and 2-hydroxyindole-3-propionic acid reveals a definite
" family " resemblance.   There are present in all three spectra two
chief bands, thyroxin showing a small but definite band at 2750 Å.U.
Table I shows the comparative relationships of the two bands.   The
" head " of a band represents the point of maximum absorption, the
" base " the point of least absorption, the difference between the
coefficients of these two points being the " persistence " of the band.

TABLE I.

Substance.	Band in the region 2500—3300 Å.U.				Band in the region 2100—2300 Å.U.	
	Ext. coef. of head × 10⁻⁴.	Wave-length. Å.U.	Ext. coef. of base × 10⁻⁴.	Wave-length. of base.	Ext. coef. of head × 10⁻⁴.	Wave-length.
Thyroxin	4·5	3275	2·5	2950	35	2275
Tryptophan ...	5·75	2750	0·1	2425	35	2200
2-Hydroxyindole 3-propionic acid	5·6	2500	0·2	2280	24	2140

With regard to the region 2500—3300 Å.U., the absorption coefficients are of the same order of magnitude, and the bands occur in the same region of the spectrum within 700 Å.U. In thyroxin, as might be expected, the bands are shifted more towards the red, and the persistence of the band is diminished, although to an extent apparently greater on account of the logarithmic notation used in plotting the absorption coefficients.

The band in the extreme ultra-violet has shown little shift towards the red, and the order of magnitude of the absorption coefficients is the same. In thyroxin, the iodine has undoubtedly shifted both bands, but one more than the other, the effect of " spreading " of the curve being noticed. The break in the curve at 2750 Å.U. seems to be due to a definite band, but owing to the experimental difficulties experienced in using such small amounts of material, it is not intended to attempt more than general comparisons from the results.

It would appear that there is a definite group resemblance, and that the indole type of curve as mapped by Ward (*Biochem. J.*, 1923, **17**, 6) is present in thyroxin. Owing to the measurements being pushed further into the ultra-violet, the second band, not plotted by Ward, was found to be present, first in thyroxin, and later in the other compounds studied.

Although an indoline derivative, the effect of substitution of iodine in the molecule, on the bands, is of interest, showing, but to a less degree, the effect first indicated by Hartley (J., 1881, **39**, 165; 1885, **47**, 693; 1903, **83**, 244), namely, a shift towards the red. The band at 4200 Å.U. moves to 4400 Å.U. and the extinction coefficient is reduced slightly. The band at 2400 Å.U. moves to 2500 Å.U., whilst that at 3000 Å.U. moves to 3075 Å.U., its persistence being at the same time reduced (compare thyroxin). The curve is spread, and all the effects seen in thyroxin are demonstrated, though to a lesser degree. Although considered by Ward to show no relation to the indole type of curve, the isatin curve does, between 3500 Å.U. and 2500 Å.U., bear a definite similarity, both in absorption coefficient and in wave-length.

Derivatives of tryptophan and thyroxin are now being studied, with a view to complete this survey, and to elucidate the formation of the " open ring " form of thyroxin postulated by Kendall (*J. Biol. Chem.*, 1919, **40**, 284), as well as to determine whether the reduced ring type of compound will give the indole type of curve.

Summary.

(1) The primary object of the investigation was to ascertain what relation, if any, exists between tryptophan and thyroxin.

(2) The absorption curves for these substances are related sufficiently to warrant the conclusion that the indole skeleton is present in thyroxin.

(3) Whether the indole type of curve will persist when the benzene ring portion of the molecule is reduced is to be further determined.

I have to thank Professor Sir F. Gowland Hopkins for placing the necessary apparatus at my disposal, and for his interest and advice during the research of which this forms a part. I am also indebted to Dr. E. C. Kendall, of the Mayo Foundation, for the specimen of 2-hydroxyindole-3-propionic acid used in the investigation, which has been conducted during the tenure of a Beit Memorial Fellowship for Medical Research.

CX.—*The Effect of Colloids in the Displacement of Lead and Copper from their Salts by Zinc.*

By LEONARD THOMAS MILLER GRAY.

ALTHOUGH the influence of addition agents in electro-plating has been the subject of many investigations, only one reference to the effect of colloids on the chemical replacement of metals, apart from studies in the preparation of sols in the presence of protective colloids, has been found. Freundlich and Fischer (*Z. Elektrochem.*, 1912, 8, 885) investigated the effect of dipping a zinc rod or immersing a zinc plate in nearly saturated solutions of certain lead salts with and without the addition of 0·04% of gelatin. They concluded that the addition of gelatin gave finer crystals, and that since the solutions were neutral and nearly saturated, this effect was due rather to conditions of crystallisation than to electrical influence of a secondary kind.

It was thought that more systematic, investigations on these lines might throw some light on the mechanism of the effect of colloids in electrolysis.

EXPERIMENTAL.

(1a) *Lead and Gelatin.*—In the first experiments strips of thin zinc foil approximately $2 \times \frac{3}{8}$ in. were suspended just below the surface of the liquid by threads, but were afterwards allowed to float on the surface. The concentration of the lead salt used (acetate) was kept very low by filling a 4 c.c. pipette with a saturated solution of the salt, the top of the pipette being just above the

surface of the water in the vessel, and allowing this to diffuse
through 200 c.c. of water before it reached the zinc foil floating
on the surface. All the experiments were carried out at room
temperature. The deposits were tested for crystal form under the
microscope (magnification 40 diameters), and for grittiness and
cohesion by rubbing between the fingers (the " tenacity " of Marc,
Z. Elektrochem., 1912, **19**, 431). For the latter test the deposits
were arranged haphazard, so as to eliminate as far as possible the
personal element. The concentration of the gelatin (Nelson's
No. 1) was varied from 0·005—2·0%.

The crystal structure of the deposit changed steadily from very
fine needles to small nodules of increasing size as the percentage
of gelatin increased from 0 to 0·3—0·4. When this proportion of
gelatin was exceeded, the size of the compact nodules diminished,
and the nodular structure was replaced by a branched structure,
the deposit, on disintegration, closely resembling the original small
needles.

The second test showed a similar maximum effect, but at a
slightly lower concentration of gelatin. Beginning as a mass of
tiny, closely coherent particles, an almost impalpable powder,
in absence of gelatin, the deposit became steadily more gritty and
less cohesive until a certain maximum was reached, beyond which
the grittiness diminished until, with 1% of gelatin, the powder
was as impalpable as at first. This maximum grittiness was
attained, in four series of experiments, at almost exactly the same
concentration of gelatin, 0·25—0·3%.

The term " nodules " is used to denote irregular particles, usually
recognisable as aggregations of crystals, differing little in length
and breadth. " Cohesion " is used to express the tendency of the
discrete particles to cohere, a tendency which was quite overcome
by rubbing between the fingers, so that an impalpable powder is
frequently strongly cohesive, whereas the most gritty specimens
are like grains of sand, with no cohesion between the grains.

(1*b*) *Lead and Gum Arabic.*—Two series of experiments were
carried out, the concentration of gum being varied from 0—10%,
but no maximum effect was observed. The grittiness increased
steadily with increasing concentration up to 2% of gum, while
no deposit was obtained on any of the strips in solutions with over
2% of gum, even after 6 weeks' contact. These solutions of higher
concentration very rapidly became mouldy.

(1*c*) *Lead and Glue.*—A very strong Scotch glue was used, the
solution of which in water reacted faintly acid to litmus. Two
series were carried out, with almost identical results. The maximum
grittiness was obtained with 0·6% of glue, and two distinct changes

of crystal structure were observed. The first took place between 0·02% and 0·05% of glue; at the lower concentration the structure still showed the needles of the pure solution, but at the higher concentration these had almost entirely given place to small nodules and branched fern structures. As the concentration of glue increased, the nodules joined together to form larger aggregations, reaching a maximum at 0·6%, the point of maximum grittiness, after which the aggregations steadily became smaller.

(2a) *Copper and Gelatin.*—A saturated solution of copper sulphate was used in the pipette, while the concentration of gelatin was varied from 0·002—1·0%. Three series were carried out, but the results in general were rather irregular owing to the fact that under these conditions copper is much more tenaciously deposited on a zinc strip than is lead, so that in many cases the tests for grittiness could not be made. A distinct maximum was, however, found, both for grittiness and for size of aggregates, at 0·15, 0·15, and 0·2% of gelatin respectively, in the three series.

(2b) *Copper and Glue.*—In all the previous experiments the zinc strip was in contact with the salt solution for periods of 20 to 45 days, sufficient metal for testing purposes then being at the bottom of the vessel. In this case, after 60 days, almost all the deposit clung tenaciously to the zinc strip. The test for grittiness had therefore to be abandoned and the copper deposit was examined on the zinc strip itself. The method of experiment was changed and the strip left for only a few days in contact with the solution. The rate of diffusion of copper sulphate from the pipette, and therefore the concentration of the salt, had a very marked effect on the nature of the deposit, so the pipettes were abandoned and the copper sulphate was added directly to the liquid to give a known concentration. As the strip frequently became incrusted with a deposit, turquoise blue or white (presumably basic salts), boric acid was added to the solution, with satisfactory results. The object of this series now became the production of the best deposit of smooth bright copper on the strip, this being judged by the naked eye and by the effect of burnishing.

Influence of concentration of copper sulphate. This was varied from 0·0002—0·0069M. The lower concentrations gave a closely adherent film, usually brownish-black, but frequently having a pink tinge. At the highest concentrations the film was similar in colour, but not so adherent, while the edges of the strip were incrusted with large globules of black copper. Strongly adherent films of bright copper were obtained with concentrations of 0·0020—0·0026M. These could be burnished and took a high polish.

Influence of concentration of glue. The concentration of copper

sulphate producing the best deposit was apparently independent of the concentration of glue and of other factors, but the concentration of glue required to give the best deposit varied considerably with the other factors.   The glue solution when freshly prepared was very sensitive, and was readily coagulated by the copper sulphate.   This sensitiveness usually disappeared on ageing for 24 hours, but the solutions coagulated at once if kept at too high a temperature, say above 25°.   The concentration required to give the best deposit varied with the time of contact; e.g., in a series of experiments under exactly the same conditions the best deposit was obtained after 2 days with 1·05% of glue, after 4 days with 1·2%, and after 14 days with 1·5%.   Of these three deposits, that obtained after 4 days was the best on burnishing.   In all cases there was a distinct deterioration in the deposit after 10 days' contact with the solution.

In general, a loose, dark deposit was obtained at low concentrations of glue.   The brightness and tenacity attained a maximum at a concentration of glue varying from 0·6% to 1·5% according to the time of contact, size of zinc strip, etc.; the brightness then decreased steadily, but not the tenacity.

Influence of boric acid.   The best deposits were obtained with 0·6—0·8% of boric acid, becoming distinctly poorer as the concentration approached 1%.

Influence of zinc strip.   Mechanical cleaning with fine emery paper gave better results than treatment with acid or alkali.   With large strips, the best deposit was produced at a smaller concentration of glue than with small strips, other conditions being the same.

Discussion.

Investigators of the influence of addition agents in electrolysis have as a rule noted no such maximum effect as has now been described, but most of their experiments were prolonged only until further addition of colloid ceased to be beneficial, and not until further addition became actually detrimental.   Kern (*Trans. Amer. Electrochem. Soc.*, 1920, **38**, 143) found a maximum when using gelatin in the refining of tin.   The fact that gum arabic shows no such maximum is in accord with the results of Isgarischev (*Koll. Chem. Beihefte*, 1921, **14**, 25), who showed that a maximum increase of polarisation is given by 0·025% of gelatin and by 2% of gum arabic, these figures being approximately in the same relation as the respective gold numbers.   Since there is a close connexion between the protective effect of colloids and the increase of polarisation (Marc, *loc. cit.*, and other investigators), gum arabic might

be expected to show a maximum in these experiments at about 20%, *i.e.*, above the experimental limits.

The generally accepted effects of colloids in electrolysis are decrease of (*a*) crystal size and (*b*) cohesive power. In these experiments with lead the size of the component crystals apparently diminishes fairly steadily throughout, but the cohesive power, by which these crystals form larger aggregates, increases up to a certain point and then diminishes. Now, it is quite conceivable that a very thinly adsorbed film of colloid may exercise a certain cohesive power, whereas when the colloid concentration is higher this film becomes thicker, and is a source of weakness and not of strength in the

In the copper experiments with glue, the decrease in size is apparently the decisive factor. The deterioration of the deposit with time of contact would then be due to the continued adsorption of colloid on the surface of the copper crystals after the zinc strip has been covered by copper, and the chemical action practically stopped. With a higher concentration of glue the whole process would be slower and the deposit would contain a higher proportion of adsorbed colloid.

Since Isgarischev (*loc. cit.*) detected a change in the viscosity curve of his solutions corresponding to the critical concentration of gelatin, a number of viscosity experiments were made. The curves obtained were quite smooth. There is therefore no indication of the formation of compounds between colloid and ions.

I desire to express my thanks to Professor A. J. Allmand for suggesting this research and for his constant help and advice during its course.

CXI.—*The Surface Tensions of Aqueous Phenol Solutions. Part I. Saturated Solutions.*

By ARTHUR KENNETH GOARD and ERIC KEIGHTLEY RIDEAL.

The Drop-weight Method of Determining Surface Tension.

THE theoretical formula for the maximum weight of a cylindrical drop hanging from a tube, in equilibrium, is

$$W = \pi r \sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where W = the weight of the drop, r = the radius of the tube, and σ = the surface tension (compare Worthington, *Proc. Roy. Soc.*,

1881, **32**, 362; *Phil. Mag.*, 1884, 1885, and Rayleigh, *Phil. Mag.*, 1899, **48**, 321).

If the detachment of the drop be considered to follow immediately, this formula would lead to the result that, *ceteris paribus*, W is proportional to r, a "law" previously discovered empirically by Tate (*ibid.*, 1864, **27**, 176). Rayleigh, however, showed (*loc. cit.*) that in practice equation (1) has to be modified; π has the value 3·8, as an approximation, for tubes of moderate radius; if r be either very small or very large, the "constant" rises well above 4; it is nowhere strictly constant.

This variation is of course due to the fact that the actual detachment of the drop is an extremely complex dynamical process (compare Perrot, *J. Chim. phys.*, 1917, **15**, 164). An attempt to derive an adequate theoretical formula has been made by Löhnstein (*Z. physikal. Chem.*, 1908, **64**, 686), but his results cannot be said to be entirely satisfactory. On the other hand, Morgan and his co-workers (*J. Amer. Chem. Soc.*, 1908—1913) have published a large number of papers in support of "Tate's Laws," claiming that under suitable conditions $W = Kr\sigma$, where K is a constant. This view, however, cannot be substantiated.

An empirical correction curve has been determined by Harkins and his co-workers (*ibid.*, 1916—1922), who have compared the surface tensions, measured by the capillary rise method, with the drop weights of water and other liquids, using dropping tubes of varying bores. The experiments, which are virtually repetitions of those of Rayleigh under improved conditions and over a greater range, are probably very accurate, but the theoretical portions of Harkins's papers leave something to be desired. For example, the relation between surface tension and drop-weight [using the same notation as in (1) above] is expressed by the equation

$$W = 2\pi r\sigma\phi \quad\quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ϕ is the empirical correction factor. A drop for which ϕ is unity is called by Harkins an "ideal drop." This term is open to the objection that equation (2) has no meaning whatsoever, theoretical or practical.

A return to a more rational expression of the relation between drop-weight and surface tension has been made by Iredale (*Phil. Mag.*, 1923, **45**, 1088). This expression rests on the fact that different liquids may form drops of similar shape from tubes of different diameters. From this, and from the assumption that rupture occurs at the point of maximum concavity, the equation

$$K_2 = \sigma_1\rho_2/\sigma_2\rho_1 \quad\quad . \quad . \quad . \quad . \quad . \quad (3)$$

is developed, where σ_1, σ_2, and ρ_1, ρ_2 are the surface tensions and

densities, respectively, of two liquids and K_2 is the ratio of the radii of the tubes from which they hang. All that is required for the practical determination of surface tension from this formula " is a knowledge of the tube-radius and drop-radius ratio, with a continuously varying radius of tube, for some standard liquid of known surface tension and density " (Iredale, *loc. cit.*).

The method of evaluation, and the table of values calculated from the data of Harkins and Brown given by Iredale have been employed by us.

In the second of two papers published in 1907, Antonov (*J. Chim. phys.*, 1907, **5**, 372) laid down the following rule :

" If A and B be two partially miscible liquids, the surface tension at the surface of contact of the two equilibrium liquid layers is equal to the surface tension of A saturated with B, less the surface tension of B saturated with A."

Data confirming this rule were given for three systems : water and (*a*) *iso*butyric acid, (*b*) ether, (*c*) benzene. The only other paper bearing on Antonov's rule seems to be one published by Reynolds (J., 1921, **119**, 466), who studied six systems : water and (*b*) ether, (*c*) benzene, (*d*) chloroform, (*e*) carbon tetrachloride, (*f*) nitrobenzene, (*g*) aniline. The rule is restated by Reynolds as a result of his observations, though no reference is made to its original author. We may take it that it is proved, at least to a first approximation, although the experiments quoted are not of a very high order of accuracy.

The system phenol–water has been studied by Whatmough (*Z. physikal. Chem.*, 1902, **39**, 129) and by Morgan and Evans (*J. Amer. Chem. Soc.*, 1917, **39**, 2151). Here the interfacial surface tension is so small that it is difficult, if not impossible, to determine it directly. Work has therefore been confined to the determination of the surface tensions of the two liquid phases; in Morgan's paper, Antonov's rule is more or less tacitly assumed.

Whatmough studied the surface tensions of the two phases from room temperature to the critical solution point; he found that the difference of surface tension decreased from about 0·5 dyne/cm. at 20° to zero at the critical solution temperature; *the surface tension of the water-rich phase he found to be higher than that of the phenol-rich phase throughout.*

Morgan, on the other hand, who worked from 15° to 55°, found that the phenol-rich phase had the higher surface tension at room temperature. His surface tension–temperature curves were approximately straight lines for both phases; *instead of converging towards the critical solution temperature* (68·8°), *however, they crossed at* 40—45°, *diverging again up to the highest temperature studied*

(55°). Commenting on this divergence, Morgan remarks—" It is evident . . . that the region studied represents the straighter portion of a curve for both layers, and instead of diverging more and more [*i.e.*, above 45°], as would be indicated by an extrapolation from the linear equations, the values for the two layers, somewhere between 55° and 68·8°, where the change in concentration in each with the temperature has become excessive, begin to approach each other again, to meet and become identical at 68·8°." This supposed formation of a loop by the surface tension–temperature curves is unsupported by any experimental evidence; it is, of course, based on the fact that the surface tension of the two layers must become identical at the critical solution temperature.

This remarkable result does not appear to have been either confirmed or challenged. That Morgan's conclusions, and also those of Whatmough, were based on experimental error can be demonstrated by the following simple qualitative test : If a two-phase mixture of water and phenol be allowed to stand in a test-tube, it will be observed that the meniscus at the surface of separation of the two liquid phases is convex towards the water-rich phase. In other words, the angle of contact with glass made by the phenol-rich phase is greater than a right angle. If, now, a capillary tube be inserted into the mixture, of such a length that its upper end lies below the liquid–air interface, the meniscus at the liquid–liquid interface will be found to be *depressed* in the capillary tube below the level of the interface outside the capillary. The interfacial tension is small, but owing to the small density difference between the two phases, the depression is considerable. This experiment was performed by us at six different temperatures ranging from 20° to 66°, with a similar result in each case. It follows, therefore, that the surface tension of the phenol-rich phase is greater than that of the water-rich phase at all temperatures from room temperature up to the critical solution point; and that Morgan's " inversion point " does not exist. These results were fully confirmed by the following quantitative measurements.

Experimental.

The drop-weight apparatus employed was that described by Bircumshaw (J., 1922, **121**, 887), the radius of the tube being 0·32161 cm. Instead of the method of " blank drops," the receiving vessel, containing a little of the liquid under investigation, was weighed before each experiment, the vessel being closed with a glass stopper. This method was employed by Morgan and was quite satisfactory. Loss of weight through evaporation was estimated by blank experiments.

The Surface Tension of Pure Water.

The values 0·9148, 0·9146 g., corrected for evaporation, for the weight of ten drops of water were obtained at 20°. With a tip of the radius mentioned, it may be calculated that Harkins would have obtained the value 0·9113 g. Thinking that this difference might be due to too rapid dropping (although our average rate was similar to that recorded by Harkins), we made an experiment in which more than 30 minutes were taken to form 10 drops. The weight obtained was 0·9120 g.; owing, however, to excessively long immersion in the thermostat, the extra loss from evaporation became considerable, a blank experiment showing this to be about 0·002 g., thus bringing the true weight practically up to the former values. The surface tension, calculated from these results by Iredale's method, is 73·06 dynes/cm. instead of 72·80. Harkins, in the preparation of his water, was very careful to avoid saline impurities; but these have a very small effect (*e.g.*, to raise the surface tension of water by 0·2 dyne/cm. the salt concentration would have to be of the order of $N/10$) compared with the possible *lowering* of surface tension by grease contamination. However clean containing vessels may be, pouring water into and from them in the air is quite sufficient to cause considerable contamination. In the authors' experiments, a column of distilled water was stored for some days in a vessel from which the water was liberated at the bottom, ensuring freedom from grease, since the latter rises to the upper portion of the column on standing. This probably accounts for the slightly higher value of the surface tension obtained. This does not preclude the probability of Harkins's results being correct among themselves; all that is necessary in calculating values from Iredale's table is the assumption that Harkins employed throughout a standard liquid of surface tension 72·800 dynes/cm.

The Surface Tension of Phenol Solutions.

The surface tensions against air saturated with vapour of the two liquid phases of the phenol–water system were determined at 0°, 17°, 30°, and 40°. Pure medical phenol was used. Certain special experimental difficulties were encountered, which will be briefly described, since the unsatisfactory results of previous workers were probably due to faulty procedure. In Morgan's experiments, for example, the containing vessel held both phases, being raised or lowered in order to measure the surface tension of lower and upper phases, respectively. This is undesirable, for reasons which will be apparent.

The persistency of emulsions in the aqueous layer has been observed by all who have worked with this system. If a sufficient

volume of both phases be taken, however, the upper portion of the aqueous layer becomes clear after some hours, the emulsion sinking towards the surface of separation. The following procedure was therefore adopted :

(1) At 0°. A glass-stoppered bottle containing about 100 c.c. of each phase was immersed in a bath of melting ice, and shaken thoroughly at short intervals for some hours. It was surrounded with melting ice and kept over-night in an ice-box. Some of the two layers was then removed by means of a pipette, cleaned and dried before each operation. By closing the upper end of the pipette with the finger, and warming the middle of it with the hand, it was possible to ensure that none of the upper layer of liquid entered the pipette during its insertion into the bottle.

The liquids thus separated were transferred to stoppered bottles, and could then be introduced separately into the drop-weight apparatus, which was immersed in a large glass tank filled with melting ice, stirred vigorously.

(2) At 17°. The procedure was similar, except that a thermostat was employed instead of an ice-bath.

(3) At 30° and 40°. A thermostat was employed; at these temperatures the operations of saturation and transference of the layers to stoppered bottles could be completed in one day. An important difficulty arose during the determination of the surface tension of the phenol-rich phase at 40°. Owing to the fact that the liquid was unavoidably cooled somewhat during the setting up of the apparatus, separation occurred. The aqueous phase which separated, having the lower surface tension, tended to line the inner surface of the capillary tube, and traces of it could not be removed by drawing the liquid backwards and forwards through the tube. It was found necessary to clean and dry the capillary tube before each experiment, and to warm the phenol-rich phase in the containing cup above 40° before placing it in position and immersing the whole apparatus in the thermostat. By this means separation of the aqueous phase was avoided, and measurements could be taken as soon as the liquid in the containing cup had cooled to 40°.

The densities of the two phases were determined by means of a pyknometer. Three determinations of the weights of twenty drops were made with each phase at each temperature; two typical results are given below :

	Wt. (g.) of 20 drops.			Max. diff. (g.).
Temp. 0°. Water-rich phase	1·0249,	1·0249,	1·0229	0·0020
Temp. 17°. Phenol-rich phase	0·9979,	0·9979,	0·9985	0·0007

At 40° the variation from the mean value amounted to $\pm 0·15\%$; owing to the very small difference between the drop weights of

the two phases, it was not practicable to work at temperatures higher than this.

The following table gives the results, the drop weights being corrected for evaporation.

Temp.	Phase.	Density.	Mean drop-wt. (g.).	Surface tension (dynes/cm.).
0°	(a) Phenol-rich	1·9685	0·05162	41·81
,,	(b) Water-rich	1·0085	0·05122	41·48
17	(a)	1·0537	0·04995	40·45
,,	(b)	1·0060	0·04963	40·19
30	(a)	1·0442	0·04877	39·50
,,	(b)	1·0025	0·04852	39·30
40	(a)	1·0332	0·04802	38·91
,,	(b)	0·9990	0·04782	38·75

The surface tension–temperature curves are convex towards the temperature axis, the convexity increasing somewhat as the temperature rises. The differences between the surface tensions of the two phases are shown in the accompanying curve, plotted against temperature. It is evident that extrapolation of the curve would give zero difference of surface tension somewhere between 60° and 80°.

FIG. 1.
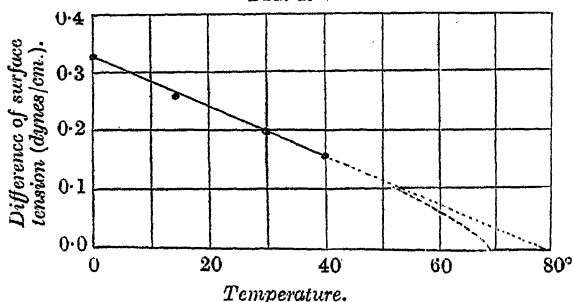
Temperature.

The results therefore confirm quantitatively those of the qualitative experiment previously described, and indicate that there is no point below the critical solution temperature at which the difference of surface tension becomes zero.

Comparison with other Systems.

There appears to be a general relation between the difference of surface tension between two such phases and their tendency towards complete miscibility. The following data illustrate this point :

Systems Water and	Diff. between S.T. of two phases.	Temp. of complete miscibility.
Benzene	34·4 dynes/cm.	
Nitrobenzene	24·7 ,,	Reynolds
Aniline	4·2 ,,	167°
Phenol....................	0·26 (17°)	68·8 Goard and Rideal

The phenol–water system is remarkable, as the phase richer in the low-tension component has the higher surface tension.

Summary.

(1) The history of the drop-weight method of determining surface tension has been briefly discussed and reasons have been given for adopting the method of calculation proposed by Iredale. The value 73·06 dynes/cm. is obtained for the surface tension of water at 20°.

(2) Experiments have been described upon the surface tensions of the two liquid phases formed by water and phenol at four different temperatures. The difference between the surface tensions of the two phases has been shown, by quantitative measurements up to 40°, and by qualitative experiments at higher temperatures, to diminish regularly up to the critical solution temperature. Previous results by other workers have thus been proved incorrect. No " inversion point " at 40—45° would appear to exist.

(3) The difference between the surface tensions of phases of this type seems to decrease with the tendency of the two liquids forming them to become completely miscible.

LABORATORY OF PHYSICAL CHEMISTRY,
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CXII.—*The Photosensitive Formation of Water from its Elements in the Presence of Chlorine.*

By RONALD GEORGE WREYFORD NORRISH and ERIC KEIGHTLEY
                          RIDEAL.

IN recent years the photochemical reaction between hydrogen and chlorine has received much attention from physical chemists, and as a result accurate data have now accumulated which enable a tolerably complete theory of this complicated reaction to be established. In general, it has been found that the presence of impurities exerts a very marked influence on the course of the reaction, manifesting itself in the period of induction, originally discovered by Bunsen and Roscoe (*Phil. Trans.*, 1857, **147**, 381), and thought by them to be a primary attribute of the reaction. Distinct from the action of foreign substances in producing the induction period, is the anticatalytic effect of oxygen, which has been shown to be related in a very simple way with the oxygen concentration both by Bodenstein and Dux (*Z. physikal. Chem.*, 1913, **85**, 297) and by Chapman and MacMahon (J., 1909, **95**

135). They have shown that the velocity of hydrogen chloride formation is inversely proportional to the concentration of oxygen, or $d[\text{HCl}]/dt = k/[\text{O}_2]$, for constant pressures of hydrogen and chlorine. It was early thought that this action of oxygen was to be attributed to some property it possessed of deactivating chlorine molecules excited by the absorption of radiation (Chapman and Underhill, J., 1913, **103**, 496), but no mechanism was postulated until M. C. C. and D. L. Chapman suggested (J., 1923, **123**, 3062) that it was connected with the formation of water. As long ago as 1907 Weigert (*Ann. Physik*, **24**, 55, 243) had shown qualitatively that a large quantity of water is produced when a mixture of hydrogen, chlorine, and oxygen is exposed to visible radiation, and it seems curious that no one had connected this fact with the anti-catalytic effect of oxygen upon the hydrogen chloride reaction. It occurred to the present authors that such a connexion must exist, and the research described in this paper has been carried out in order to obtain quantitative information upon the reaction of Weigert, with a view to discovering the mechanism, and tracing its connexion, if any, with the kinetics of hydrogen chloride formation.

By means of the apparatus described below, it was possible to bring hydrogen, chlorine, and oxygen in any desired proportions into a reaction tube containing phosphorus pentoxide in a thermostat, and the rate of formation of water, upon illumination of the mixture by visible radiation only, could be measured by observing the rate of change of gaseous pressure as the water formed was absorbed. The total pressure of the reactant gases was maintained initially at 70 cm. of mercury, and, under the most favourable conditions of water formation, fell by about 3 cm. of mercury in 30 minutes, so that the reaction was virtually carried out at constant pressure. The rate of formation of water was independent of hydrogen pressure over the very wide range investigated, *i.e.*, from 0·16 to 0·9 of the total pressure, and was proportional to the product of the chlorine and oxygen concentrations, or

$$d[\text{H}_2\text{O}]/dt = k[\text{O}_2][\text{Cl}_2].$$

In this respect, the mechanics of the reaction are similar to the photosensitive action of chlorine upon the decomposition of ozone by visible radiation studied by Bodenstein and Bonhoeffer (*Z. Physik*, 1923, **13**, 94), who found that the velocity of decomposition was given by the relationship $- d[\text{O}_3]/dt = k[\text{O}_3][\text{Cl}_2]$.

Both these expressions are consistent with the hypothesis that the reactions in question are brought about by the catalytic influence of chlorine molecules activated by radiation, and thus, together with the activation of hydrogen by resonating mercury atoms, discovered by Cario and Franck (*ibid.*, 1922, **21**, 161), these reactions may be

classed as the simplest cases of photochemical sensitisation. They are possibly comparable with the numerous cases of optical sensitisation of the photographic plate produced by impregnation of the silver salts with organic dyestuffs.

EXPERIMENTAL.

The reaction chamber (Fig. 1) consisted of a glass tube, A, 34 cm. long, 2 cm. in internal diameter, and of about 100 c.c. capacity, which had been carefully cleaned with chromic acid and distilled water, and dried. A small quantity of phosphoric acid was placed

FIG. 1.

PLAN
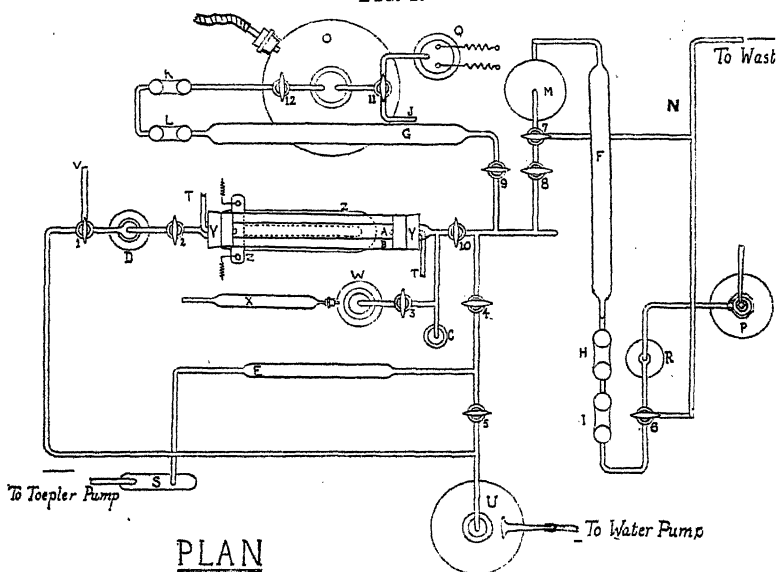
along the bottom of the tube. The reaction tube was jacketed by a wide tube, B, 5 cm. in diameter, and the rubber stoppers, Y, Y. A rapid stream of water was circulated through this outer tube from a thermostat by way of the tubes S, T, by means of a pump. A preliminary evacuation of the reaction tube could be effected by opening taps 10, 4, and 5, thus effecting communication with a water-pump. The evacuation could then be completed after closing 5, by means of a Toepler mercury pump, which communicated with the apparatus through a tube, E, containing caustic soda, and finally closing tap 10. The hydrogen–oxygen mixture was prepared by adding either pure hydrogen or oxygen to electrolytic gas, and was stored in the aspirator, O. By opening taps 12 and 9, and then 10 very carefully, the mixture was passed into A,

by way of the U tubes K, L, containing soda-lime and calcium chloride respectively, and the tube G, containing phosphoric oxide sprinkled on glass wool. When the required partial pressures of hydrogen and oxygen had been obtained in A, as registered by the vertical mercury manometer, C, the connecting tube between taps 10, 9, 8, and 4 was re-evacuated by the water-pump by opening 5 and 4. This connecting tube was then filled with chlorine by shutting 4 and expanding the gas from the chlorine container, M, by way of taps 7 and 8. Evacuation and refilling with chlorine were carried out in this way three times, and then the chlorine in the container M was allowed to expand by way of taps 7, 8, and 10 into A until a total pressure of 700—720 mm. was registered on the mercury manometer. The chlorine container, M, consisted of a large vessel of 1500 c.c. capacity which was kept filled with chlorine by allowing a constant stream to flow through from the liquid chlorine cylinder, P, by way of the water bubbler, R, the two-way tap 6, the U tubes I and H (containing calcium chloride), the drying tube F (containing phosphoric oxide), the tap 7, and to waste through the tube N. When it was desired to use the chlorine in M, the stream from the cylinder was diverted to waste by turning tap 6 in communication with N, and putting 7 into communication, *via* 8 and 10, with the reaction chamber.

When these conditions for filling the tubes were observed, *i.e.*, the chlorine being put in last, the mercury in the vertical mano-meter, C, was not affected by the chlorine for generally over an hour, it being protected by a layer of hydrogen and oxygen. A new mercury manometer was fused on for each experiment.

During the preparation of the required mixture of the three gases, the double-barrelled, quartz mercury vapour lamp, Z, placed vertically below A and effectively screened, was allowed to run in order to get to a steady state of burning. The lamp was worked off a 220 volt circuit and carried a current of 4·5 amps. Its distance from the reaction chamber was kept constant at 8 cm. below the outer tube, B.

By moving the screen between the lamp and the tube B, the mixture of gases in A could be exposed directly to the visible radiation of the quartz. lamp, the ultra-violet radiation being absorbed by the glass walls of the vessels A and B. The first effect observable upon illumination was an immediate increase of pressure occasioned by the Draper effect, which seemed roughly to be pro-portional in magnitude to the square of the chlorine concentration. After about $\frac{1}{4}$ minute, the pressure began to fall off, and after 1 or 2 minutes the rate of decrease became regular as the water formed was absorbed by the phosphoric oxide.

Two series of preliminary experiments were carried out in order to ensure that no reduction of pressure occurred through the absorption of hydrogen chloride by the dry phosphoric oxide.

In the first case, pure hydrogen and chlorine were enclosed in the reaction tube and illuminated. A preliminary expansion (Draper effect) always occurred, but no subsequent fall of pressure, showing that the hydrogen chloride formed was not appreciably absorbed. This experiment was carried out at intervals throughout the work as a test of the efficiency of the phosphoric oxide, and it was always found that so long as no moisture was observable on the phosphoric oxide no absorption of hydrogen chloride occurred. The phosphoric oxide in the reaction tube was always replaced after every four or five experiments, so that dry material was always used, although it was found in general to be efficient for some eight or nine experiments.

As a second check that no hydrogen chloride or chlorine was absorbed by the drying agent, the total combined and uncombined chlorine in the gaseous phase after illumination was estimated and compared with the quantity of chlorine initially put in, estimated from pressure–volume measurements. In these experiments electrolytic gas–chlorine mixtures were used, and a decrease of pressure due to the formation of water was always observed. The chlorine in the gaseous phase after illumination was estimated by drawing the gases out of the chamber *via* stopcocks 1 and 2 by means of the water-pump through potassium iodide solution contained in the wash-bottle, D (Fig. 1). The free chlorine liberated iodine, whilst the hydrogen chloride was dissolved, so that the total chlorine could be obtained by successive titrations with standard sodium thiosulphate and standard caustic soda. From the following figures (Table I), it will be seen that the chlorine initially put

TABLE I.

Volume of reaction chamber = 110 c.c.

Pressure of electro-lytic gas in mm. of Hg.	Pressure of chlorine in mm. of Hg.	Chlorine (g.) estimated at end of exposure.		Total Cl (g.) estimated at end.	Total Cl_2 (g.) put in initially.	Diff (g.).
		(a) As HCl.	(b) As Cl_2.			
688·5	30·3	0·00924	0·00248	0·0117	0·0129	−0·0012
649	78	0·0264	0·00603	0·0325	0·0334	−0·0009
582	128	0·0480	0·0073	0·0553	0·0553	0·0000
456	250	0·0970	0·0122	0·1092	0·1075	+0·0017
277·5	414·5	0·0618	0·1183	0·1801	0·1775	+0·0026

into the reaction chamber can be accounted for at the end within the accuracy of the experimental method, proving that no appre-

ciable absorption of either hydrogen chloride or chlorine by the drying agent occurs under the conditions obtaining in these experiments.*

Fig. 2.
Pressure of Cl_2=ca. 110 mm.

Fig. 3.
Pressure of Cl_2=ca. 55 mm.

Total pressure of gases=700 mm.
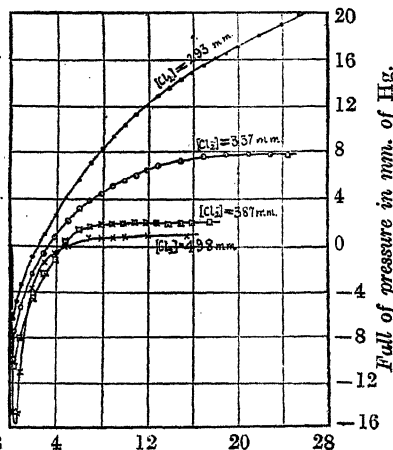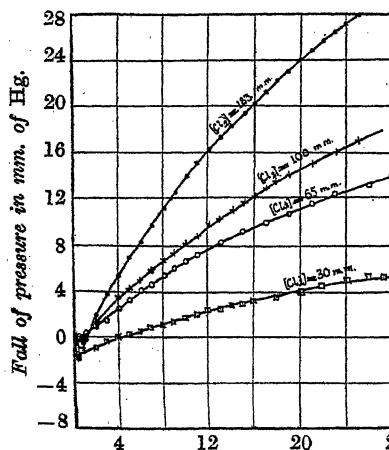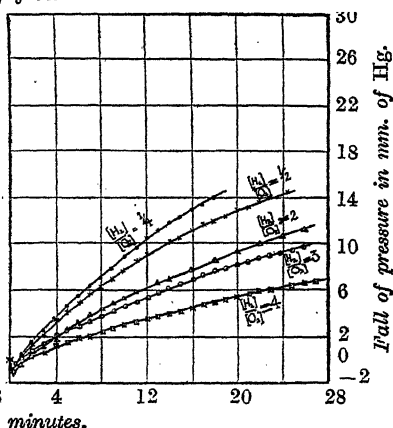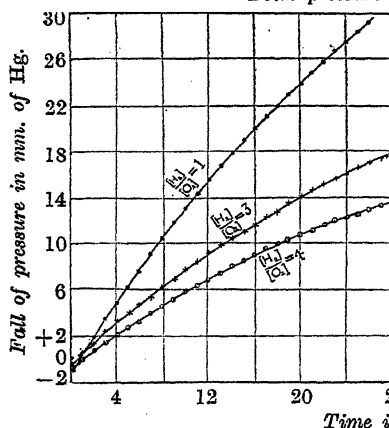
Time in minutes.

Fig. 4.
Medium and low pressures of chlorine.
$[H_2]/[O_2]=2$.

Fig. 5.
High pressures of chlorine.
$[H_2]/[O_2]=2$.
Large Draper effects.

Time in minutes.

Even if the small irregular differences shown in the last column are real, they yield, when put in terms of pressure change, figures

* For pressures of hydrogen chloride of 500 mm., a small decrease in volume was observed after 24 hours' contact with phosphorus pentoxide.

which are small compared with the actual pressure change recorded due to water formation, and in general do not vitiate the results by more than $\pm 5\%$. It is believed, however, that the pressure change observed gives the water formation to a closer degree of accuracy than this, since it has already been shown above independently that hydrogen chloride or chlorine absorption does not take place under the present conditions of experiment.

These preliminary experiments having established this fact, a large number of experiments were carried out with hydrogen and oxygen in ratios ranging from 4 to $\frac{1}{4}$ and chlorine in varying proportions. A large number of curves, of which those in Figs. 2 to 5 are characteristic, were obtained, in which fall of pressure is plotted against time in minutes. These curves show, in nearly all cases, a preliminary increase in pressure due to the Draper effect, which lasted for about 1 minute, and thereafter a regular fall in pressure due to the absorption of the water produced. The rate of fall of pressure gradually decreases as the reaction proceeds to completion, but by taking the initial slope of the curves after the first 2 minutes, when the system has recovered from the Draper effect, we obtain a measure of the rate of formation of water. This slope is defined as the " water sensitivity " of the reaction mixture and is directly proportional to the initial rate of formation of water. In general, the slope could be determined very accurately, since for several minutes after the start the rate of fall of pressure remained uniform.

In the cases where the chlorine pressure is large, the Draper effect is very great, since the velocity of hydrogen chloride formation to which this is proportional (Baly and Barker, J., 1921, **119**, 653) depends roughly on the square of the chlorine concentration. If at the same time the hydrogen pressure is small, the hydrogen will be rapidly used up, so that at the time the system has recovered from the Draper effect, the hydrogen pressure will be very largely reduced. For such cases (indicated by an asterisk in the tables and shown in Fig. 5), no accurate estimate of the water sensitivity can be obtained, as the pressure changes too rapidly, and the reaction is over too quickly to enable any photochemical stationary state to be established in the system.

The figures in Table II embodying the results of these experiments indicate that the water sensitivity is proportional to the product of the chlorine and oxygen concentrations, and independent of the hydrogen concentration over a wide range of hydrogen pressures, as is shown by the constancy of the figures in the last column.

TABLE II.

| Ratio [H_2]/[O_2]. | Pressure of reactant gases in mm. of mercury. | | | | Product [Cl_2][O_2] $\times 10^{-2}$. | Water sensitivity. S. | $K =$ [Cl_2][O_2]/S $\times 10^{-2}$. |
	Chlorine.	Oxygen.	Hydrogen.	Total.			
4	57	131·2	525	713	74·8	0·33	226
4	116·5	120	480	716	140	0·61	230
4	177·5	106·5	426	710	189	0·90	210
4	214	99·5	398	721	213	0·94	227
4	341	75·2	301	717	256	1·07	240
3	57	161	483	701	92	0·41	225
3	114	147	441	701	167	0·78	229
3	181	129	388	698	234	1·02	229
3	252	115	345	712	290	1·23	236
3	304·5	99·5	298·5	702·5	303	1·31	231
2	30·3	230	460	720	69·7	0·30	232
2	32	221	442	695	70·7	0·28	252
2	64	210	420	694	134	0·58	232
2	66	210	420	696	138	0·62	223
2	81	210	420	711	170	0·76	224
2	100	206	412	718	206	0·78	260
2	128	194	388	710	248	0·94	264
2	156·5	185·5	371	713	290	1·28	234
2	159·5	185	370	714·5	295	1·26	234
2	183	182	364	729	333	1·42	234
2	187	179	358	724	334	1·50	223
2	218·5	163	326	707·5	356	1·46	238
2	249	152	304	705	378	1·44	263
2	293·5	139	278	710·5	407	1·61	253
2	337	120	240	697	405	1·70	238
2	387·5	114	228	729·5	434	1·22 *	352 *
2	414·5	86	172	672·5	356	0·45 *	792 *
2	498·5	73	146	717·5	365	0·38 *	960 *
1	46·5	332·5	332·5	731·5	155	0·65	237
1	107·0	307·5	307·5	722	329	1·41	233
1	163·5	278	278	729·5	455	1·90	237
1	204·5	256	256	716·5	524	2·17	241
1	254	233	233	720	592	2·14	276
½	50	445	222	717	222	0·92	241
½	51	449	225	715	229	0·94	243
½	57	449	224	730	226	0·90	250
½	112	409	205	726	458	1·64	279
½	170	365	183	718	621	1·58 *	393 *
½	240	319	160	719	768	1·73 *	444 *
⅓	35·5	511	170	716·5	181	0·62	292
⅓	70·0	493	164	727	345	1·21	285
⅓	100	451·5	150·5	702	451	1·60	282
⅓	166·5	416	139	721·5	692	1·36*	509 *
¼	28	542	135·5	705·5	152	0·56	272
¼	37	542	135·5	716·5	201	0·68	295
¼	51	529	132	712	270	0·98	275
¼	52	532	133	717	263	1·00	263
¼	69·5	511	128	708·5	357	1·22	292
¼	98	493	123	714	482	1·51	313
¼	106	488	122	716	517	1·69	305
¼	149	451	113	713	672	1·30 *	517 *
¼	149	451	113	713	674	1·32 *	510 *
¼	209	404	101	714	845	1·38 *	612 *

Discussion of Results.

A simple explanation of the photosensitive action of· chlorine may be obtained by means of the hypothesis that chlorine molecules activated by the absorption of radiation can transfer some of their intra-atomic energy to oxygen molecules upon collision with them, thereby rendering the latter active and capable of reacting with hydrogen molecules to form water.

Let us represent the concentration of active chlorine at any moment by $[Cl_\epsilon]$. The rate of formation of these active chlorine molecules is proportional to the intensity of illumination and to the chlorine pressure, $i.e.$,

$$d[Cl_\epsilon]/dt = kI[Cl_2] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

There are two possible modes of their reversion to the non-active state :

(1) Degradation of their energy by thermal radiation.

(2) Degradation by collision with oxygen molecules and activation of the latter.

The active chlorine molecules may also be removed from the sphere of action by

(3) colliding with hydrogen molecules and forming hydrogen chloride.

(4) colliding with chlorine molecules and forming dissociated chlorine atoms capable of starting " Nernst chain reactions."

For their rate of removal, we may thus write :

$$+ d[Cl_\epsilon]/dt = k_1[Cl_\epsilon] + k_2[Cl_\epsilon][O_2] + k_3[Cl_\epsilon][H_2] + k_4[Cl_\epsilon][Cl_2] \quad (2)$$

Equating equations (1) and (2) we obtain the equilibrium quantity of active chlorine present at any moment :

$$[Cl_\epsilon] = \frac{kI[Cl_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \quad . \quad . \quad (3)$$

Denoting by $[O_\epsilon]$ the concentration of active oxygen molecules, the rate of oxygen activation is, according to hypothesis :

$$\frac{d[O_\epsilon]}{dt} = k_2[Cl_\epsilon][O_2] = \frac{kk_2I[Cl_2][O_2]}{k_1 + k_2[O_2] + [k_3][H_2] + k_4[Cl_2]} \quad . \quad (4)$$

The activated oxygen molecules may be removed either

(1) by thermal degradation of their energy

or (2) by the collision with hydrogen and formation of water.

We may thus write :

$$+ d[O_\epsilon]/dt = k_5[O_\epsilon] + k_6[H_2][O_\epsilon] \quad . \quad . \quad . \quad . \quad (5)$$

Equating equations (4) and (5), we obtain the concentration of active oxygen present at equilibrium :

$$[O_\epsilon] = \frac{kk_2I[Cl_2][O_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \cdot \frac{1}{k_5 + k_6[H_2]} \qquad . \quad . \quad (6)$$

The rate of formation of water according to hypothesis is :

$$d[H_2O]/dt = k_6[H_2][O_\epsilon] \qquad . \quad . \quad . \quad . \quad . \quad (7)$$

Hence, combining (6) and (7),

$$\frac{d[H_2O]}{dt} = \frac{kk_2k_6I[Cl_2][O_2]}{k_1 + k_2[O_2] + k_3[H_2] + k_4[Cl_2]} \cdot \frac{[H_2]}{k_5 + k_6[H_2]} \qquad . \quad . \quad (8)$$

This expression reduces to that found experimentally, namely :

$$d[H_2O]/dt = k_0[Cl_2][O_2] \qquad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

if (1) k_1 is large compared with $k_2[O_2]$, $k_3[H_2]$, and $k_4[Cl_2]$, i.e., if deactivation of chlorine takes place principally by thermal degradation, and if (2) $k_6[H_2]$ is large compared with k_5, i.e., if nearly every active oxygen molecule produced persists long enough to meet a hydrogen molecule and to form water.

This mechanism, which accounts for the formation of water as a result of the photosensitive action of chlorine, brings the process into line with the decomposition of ozone by illuminated chlorine, and with the activation of hydrogen molecules by excited mercury atoms referred to above.

Upon the present theory this formation of water is regarded as independent of the concomitant formation of hydrogen chloride. The anticatalytic effect of oxygen on the latter reaction is regarded as due to the direct intervention of oxygen in the hydrogen–chlorine reaction chains, a process which results in their shortening and possibly the production of water. This secondary formation of water is regarded as subsidiary to the primary formation by the photosensitive process described above, and there are good reasons for supposing that it is negligible compared with the latter.*

Summary.

The formation of water in the gaseous system hydrogen–oxygen–chlorine on illumination by visible radiation is governed by the relationship

$$d[H_2O]/dt = k[Cl_2][O_2].$$

It is independent of the partial pressure of hydrogen between the limits 0·16 and 0·9 of the total pressure. This result is consistent

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* It is hoped to deal with this point in greater detail in a subsequent paper on the kinetics of the hydrogen–chlorine reaction.

with the hypothesis that activation of the oxygen is first brought about by contact with chlorine molecules activated by absorption of light.

With the photosensitive decomposition of ozone by chlorine, and the activation of hydrogen by resonating mercury atoms, this reaction falls into the simplest class of photochemical sensitisation.

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CXIII.—*cyclo*T*elluropentanediones Containing Aliphatic and Aromatic Substituents.*

By GILBERT T. MORGAN and CYRIL JAMES ALLAN TAYLOR.

WHEN first discovered, the tellurium derivatives containing a bivalent β-diketonic radical were regarded as cyclic compounds containing both tellurium and oxygen in the ring. Further investigation has, however, rendered this view untenable and the experiments described below confirm the hypothesis that these substances are truly organometalloidal derivatives having a six-membered ring including one tellurium and five carbon atoms (J., 1924, **125**, 1601). The two hydrogens replaced by tellurium are derived not from the methylene group but from the terminal hydrocarbon radicals.

Dipropionylmethane furnishes a bivalent chelate group to tellurium, and condensation with the tetrachloride gives rise to 2 : 6-dimethyl*cyclo*telluripentane-3 : 5-dione 1 : 1-dichloride, which on reduction yields 2 : 6-*dimethylcyclotelluropentane*-3 : 5-*dione* (I). This substance under its former name of tellurium dipropionylmethane (J., 1924, **125**, 740) has been extensively employed in bacteriological studies, in which it has manifested the highest germicidal power of its series (*Biochem. J.*, 1923, **17**, 30; 1924, **18**, 190; *J. Soc. Chem. Ind.*, 1924, **43**, 304T). The diketonic structure implied by its new designation is demonstrated by the production of the *dioxime* (II).

In the tellurium condensation, dipropionylmethane reacts to a slight extent in its monoenolic form, yielding as a by-product tellurium O-ethyldipropionylmethane trichloride, but with 3-*methyldipropionylmethane* this tendency is inhibited and 2 : 4 : 6-*trimethylcyclotelluripentane*-3 : 5-*dione* 1 : 1-*dichloride* becomes the only telluriferous product. On reduction, this telluridichloride furnishes 2 : 4 : 6-*trimethylcyclotelluropentane*-3 : 5-*dione* (I), which also manifests its diketonic structure by forming a *dioxime* (II).

(I.)

$$
\begin{array}{c}
\text{Te} \\
\diagup \ \diagdown \\
\text{CH}_3\text{·CH} \quad \text{CH·CH}_3 \\
\text{OC} \qquad \text{CO} \\
\diagdown \ \diagup \\
\text{CHR}
\end{array}
\longrightarrow
\begin{array}{c}
\text{Te} \\
\diagup \ \diagdown \\
\text{CH}_3\text{·CH} \quad \text{CH·CH}_3 \\
\text{HON:C} \qquad \text{C:NOH} \\
\diagdown \ \diagup \\
\text{CHR}
\end{array}
$$
(II.)

R = H or CH₃
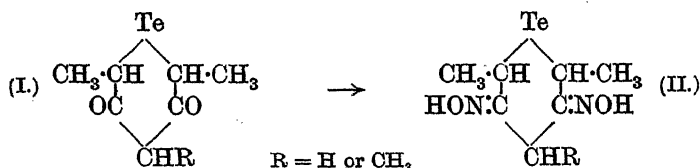
Hitherto the *cyclo*telluripentanedione dichlorides have been obtained only from exclusively aliphatic β-diketones, but this condensation has now been brought about both with 3-*benzyl-acetylacetone* and with 3 : 3-*dibenzylacetylacetone*. The two resulting *telluridichlorides* show the characteristic cyclic property of reduction to 4-*benzylcyclotelluropentane*-3 : 5-*dione* (III) and 4 : 4-*dibenzyl-cyclotelluropentane*-3 : 5-*dione* (IV), the formation of the latter substance being of special interest in confirming the observation, already made with 3 : 3-dialkylacetylacetones, that a β-diketone still furnishes a chelate group to tellurium even when both the hydrogen atoms of the methylene group have been replaced by hydrocarbon radicals.

(III.)

$$
\begin{array}{c}
\text{Te} \\
\diagup \ \diagdown \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{OC} \qquad \text{CO} \\
\diagdown \ \diagup \\
\text{CH} \\
\text{CH}_2\text{·C}_6\text{H}_5
\end{array}
$$

$$
\begin{array}{c}
\text{Te} \\
\diagup \ \diagdown \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{OC} \qquad \text{CO} \\
\diagdown \ \diagup \\
\text{C} \\
\diagup \ \diagdown \\
\text{C}_6\text{H}_5\text{·CH}_2 \quad \text{CH}_2\text{·C}_6\text{H}_5
\end{array}
$$
(IV.)
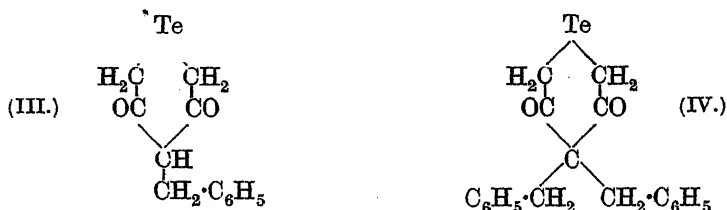
The diketonic constitution of the monobenzyl compound (III) is confirmed by the formation of its *dioxime*.

In a previous communication on tellurium derivatives of diketones (J., 1924, **125**, 731), it was shown that one terminal branched chain inhibited the formation of cyclic derivatives containing TeCl₂ linked with a bivalent chelate group.

The simplest case of a β-diketone with branched chains at both ends has now been investigated by attempting to condense tellurium tetrachloride with *di*isobutyrylmethane. This new diketone inter-acted with very great difficulty, nine-tenths of the combined tellurium was eliminated in the elemental condition, and only a very small amount of telluriferous product was obtained which had the reactions of *tellurium* O-*ethyldiisobutyrylmethane trichloride*, $(CH_3)_2CH·C(O·C_2H_5):CH·CO·C(CH_3)_2·TeCl_3$ (V). This evidence and the following data show very plainly that branching of the hydrocarbon chain rather than its length is the inhibiting factor in the production of *cyclo*telluripentanedione dichlorides.

When β-diketones containing comparatively long normal (un-

branched) chains are condensed with tellurium tetrachloride, cyclic dichlorides are obtained.

(VI.) $CH_3 \cdot [CH_2]_n \cdot CH$ CH_2 with $TeCl_2$ bridge, OC CO, CH_2 $CH_3 \cdot [CH_2]_n \cdot CH$ CH_2 with Te bridge, OC CO, CH_2 (VII.)

$n = 5$ or 6.
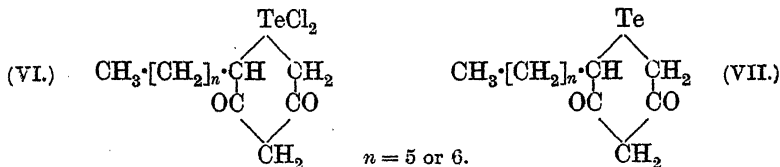
The condensation was tested on n-*octoylacetone*,

$$C_7H_{15} \cdot CO \cdot CH_2 \cdot CO \cdot CH_3,$$

and n-*nonoylacetone*, $C_8H_{17} \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$. The isolation of the dichlorides became increasingly difficult because of their greater solubility and fusibility as the series is ascended.

The reaction between *n*-nonoylacetone and tellurium tetrachloride not only furnished the cyclic dichloride (VI), but gave also a considerable proportion of *tellurium* n-*nonoylacetone trichloride*, $CH_3 \cdot [CH_2]_6 \cdot CH_2 \cdot CO \cdot CH \colon C(OH) \cdot CH_2 \cdot TeCl_3$, this being the third case observed of the formation of an enolisable trichlorotellurium derivative, the other two analogous products being derived from *n*-heptoylacetone and dibutyrylmethane (J., 1924, **125**, 738, 757).

EXPERIMENTAL.

2 : 6-*Dimethyl*cyclo*telluropentane*-3 : 5-*dionedioxime* (II, R=H).—When condensed with tellurium tetrachloride, dipropionylmethane yielded 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione 1 : 1-dichloride together with tellurium *O*-ethyldipropionylmethane trichloride as by-product. The former when reduced with bisulphite furnished 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione, which was warmed for 10 minutes with excess of partially neutralised hydroxylamine sulphate in aquo-alcoholic solution. The separated dioxime crystallised from hot dilute alcohol in pale yellow needles decomposing at 168—170° : 0·1490 gave 13·6 c.c. of N_2* at 21° and 743 mm., N = 10·15. $C_7H_{12}O_2N_2Te$ requires N = 9·88%. This dioxime is insoluble in water, although dissolving freely in aqueous caustic soda.

2 : 4 : 6-*Trimethyl*cyclo*telluropentane*-3 : 5-*dione*.

3-*Methyldipropionylmethane*, $CH_3 \cdot CH(CO \cdot C_2H_5)_2$.—Sodium dipropionylmethane was heated under reflux with excess of methyl iodide, and the 3-alkyl-diketone isolated as in a similar experiment (J., 1924, **125**, 748). 3-Methyldipropionylmethane was a colourless, mobile liquid, b. p. 92°/10 mm. (yield 10 g. from 12·8 g. of

* In this and the following nitrogen estimations the gas was moist.

dipropionylmethane). It was miscible with the ordinary organic solvents; its alcoholic solution developed a deep violet coloration with ferric chloride. The *copper* salt, obtained by the action of ammoniacal cupric acetate, crystallised from benzene in silky, grey tufts decomposing at 172—173°; it dissolved in hot petroleum (b. p. 40—60°) to an olive-green solution which, on cooling, deposited a woolly mass of grey needles : 0·4288 gave 0·0988 CuO, Cu = 18·60. $C_{16}H_{26}O_4Cu$ requires Cu = 18·36%.

When dissolved in boiling methyl or ethyl alcohol, a light blue copper salt was formed, a colour change indicating the formation of a mixed alkyloxy-copper compound, Et·CO·CMe·CEt·O·Cu·OAlk (*loc. cit.*, p. 746). Ten g. of 3-methyldipropionylmethane were heated for 2½ hours on the water-bath with 70 c.c. of purified chloroform and 9·5 g. of tellurium tetrachloride; the clear liquid was then concentrated in a vacuum desiccator, and in a few days the viscid residue yielded several crops of crystals which on recrystallisation from warm acetone were obtained in colourless needles darkening at 180°. The yield was 68% and no other telluriferous product was obtained : 0·2102 gave 0·1766 AgCl, Cl = 20·80. $C_8H_{12}O_2Cl_2Te$ requires Cl = 20·96%.

2 : 4 : 6-*Trimethyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* was sparingly soluble in the ordinary organic media with the exception of acetone. With aqueous potassium metabisulphite (2 mols.) in the cold, the dichloride was reduced almost quantitatively to 2 : 4 : 6-*trimethyl*cyclo*telluropentane*-3 : 5-*dione* (I, R = CH_3), which was slightly soluble in cold water to a yellow neutral solution having powerful bactericidal properties but much less active in this respect than the solution of 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione. The new trimethylated compound crystallised from alcohol in bright yellow needles darkening at 133° and melting with decomposition at 135° : 0·1640 gave 0·2152 CO_2 and 0·0677 H_2O, C = 35·79, H = 4·58; 0·2355 gave 0·1130 Te, Te = 47·90. $C_8H_{12}O_2Te$ requires C = 35·89, H = 4·48, Te = 47·66%.

2 : 4 : 6-*Trimethyl*cyclo*telluropentane*-3 : 5-*dionedioxime* (II, R = CH_3), prepared as in the experiment on p. 799, separated from the cooled solution in yellowish-green plates which, after extraction with hot benzene, were recrystallised from acetylacetone and separated in yellow flakes decomposing at 170° : 0·1700 gave 13·8 c.c. N_2 at 22° and 748·5 mm., N = 9·1. $C_8H_{14}O_2N_2Te$ requires N = 9·41%.

4-*Benzyl*cyclo*telluropentane*-3 : 5-*dione* (III).

Purified acetylacetone was added to the calculated quantity of sodium dissolved in absolute alcohol, when sodium acetylacetone separated in masses of glistening needles, which were dried at 60°

on porous plates. This sodium derivative (50 g.) mixed with 150 g. of benzyl chloride was heated at 160—200° for 8 hours; the reaction commenced at 120°. The filtrate from sodium chloride was distilled up to 260° to remove excess of benzyl chloride; the residue was then fractionated under reduced pressure, when 30 g. of 3-*benzylacetyl-acetone* were obtained as a colourless oil, b. p. 150°/3 mm. (yield 39%). The viscid, black, oily residue yielded subsequently 3 : 3-*di-benzylacetylacetone* (see p. 802).

3-*Benzylacetylacetone*, $C_6H_5 \cdot CH_2 \cdot CH(CO \cdot CH_3)_2$, a mobile liquid with a sharp odour, was readily miscible with petroleum, benzene, or chloroform, but not with water; its alcoholic solution gave an intense violet coloration with ferric chloride, and with ammoniacal cupric acetate it furnished the *copper* salt as a light grey precipitate, which on repeated crystallisation from benzene separated in grey needles, m. p. 176°: 0·5030 gave 0·0886 CuO, Cu = 14·1. $C_{24}H_{26}O_4Cu$ requires Cu = 14·37%. *Copper 3-benzylacetylacetone* was sparingly soluble in cold organic solvents, but dissolved in hot alcohol or benzene to green solutions from which it separated in neutral grey needles.

4-*Benzylcyclotelluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*.—3-Benzyl-acetylacetone (5·8 g.) and 2·7 g. of tellurium tetrachloride dissolved in 20 c.c. of boiling chloroform to a yellowish-red solution which darkened and evolved hydrogen chloride. After removing 0·3 g. of tellurium, the solution was concentrated under reduced pressure to a viscid glue. A portion washed with carbon tetrachloride and extracted with chloroform furnished, on evaporating off the solvent, a few white crystals, which were utilised in inoculating the main batch, about 2 g. of telluridichloride being thus obtained. The product crystallised from benzene on addition of light petroleum in white flakes decomposing at 180°: 0·2054 gave 0·1520 AgCl, Cl = 18·31. $C_{12}H_{12}O_2Cl_2Te$ requires Cl = 18·37%.

The foregoing dichloride was reduced smoothly with aqueous metabisulphite, the precipitate being crystallised by concentrating its cold benzene solution.

4-*Benzylcyclotelluropentane*-3 : 5-*dione* (III) dissolved sparingly in boiling water and readily in hot organic media, separating from alcohol in light yellow, glistening flakes; from acetylacetone solutions large, prismatic crystals were obtained, m. p. 153° (decomp.): 0·1506 gave 0·2524 CO_2 and 0·0540 H_2O, C = 45·71, H = 3·98; 0·2517 gave 0·1020 Te, Te = 40·43. $C_{12}H_{12}O_2Te$ requires C = 45·64, H = 3·81, Te = 40·41%.

4-*Benzylcyclotelluropentane*-3 : 5-*dionedioxime*, prepared as on p. 799, was precipitated as a flocculent, yellow-green mass sparingly soluble in hot benzene and separating therefrom as a yellowish-

green powder, decomposing at 168—170° : 0·1606 gave 11·75 c.c. N_2 at 18° and 735 mm., N = 8·15. $C_{12}H_{14}O_2N_2Te$ requires N = 8·10%.

Insoluble in water, the oxime dissolved in cold aqueous caustic soda to a yellow solution which deposited tellurium on boiling.

4 : 4-*Dibenzylcyclotelluropentane*-3 : 5-*dione* (IV).

3 : 3-*Dibenzylacetylacetone*, $(C_6H_5 \cdot CH_2)_2C(CO \cdot CH_3)_2$, was obtained as a by-product in the preparation of 3-benzylacetylacetone. The dark oily residue left after distilling off the monobenzyl compound was fractionated further and at 200—227°/3 mm. a distillate was obtained which solidified to a mass of acicular crystals coloured yellow by impurities, which were removed with cold ether. After two crystallisations from alcohol, it melted at 111—112° (yield 2 g. or 1·5%) : 0·0998 gave 0·2970 CO_2 and 0·0646 H_2O, C = 81·2, H = 7·19. $C_{19}H_{20}O_2$ requires C = 81·43, H = 7·14%.

This β-diketone was insoluble in water and dissolved only sparingly in cold organic solvents. It separated from ether in transparent, colourless prisms, developed no coloration with ferric chloride, and did not furnish a copper salt with ammoniacal cupric acetate. It did not condense with *p*-nitrophenylhydrazine.

3 : 3-*Dibenzylacetylacetone   from   3-Benzylacetylacetone.*—Sodium (1·6 g.), cut into thin slices, was added to 3-benzylacetylacetone (12·8 g.) dissolved in 100 c.c. of dry ether. After the metal had dissolved completely, the solution became semi-solid owing to the separation of *sodium 3-benzylacetylacetone*, a voluminous, white powder, m. p. 109°, and soluble in cold alcohol or water, reacting with cupric acetate to yield a grey copper derivative. The dry sodium derivative (25 g.) was heated with 70 g. of benzyl chloride at 200—210° for 11 hours. The precipitated sodium chloride was washed with ether. The ethereal filtrate was evaporated and distilled under reduced pressure to eliminate excess of benzyl chloride. The oily residue, inoculated with a crystal of 3 : 3-dibenzylacetylacetone, solidified to a light brown mass. When purified by crystallisation from alcohol, 10 g. of the dibenzyl compound were obtained (yield 30%).

4 : 4-*Dibenzylcyclotelluripentane*-3 : 5-*dione*   1 : 1-*dichloride*   was produced by condensing 3·3 g. of dibenzylacetylacetone with 2·6 g. of tellurium tetrachloride in 30 c.c. of pure chloroform. After 2—3 hours, the solution had darkened considerably and tellurium was deposited. The filtrate, concentrated to a small bulk, was extracted with petroleum (b. p. 40—60°) to remove unchanged β-diketone, and the oily residue left to crystallise in a vacuum desiccator. After 1 month, the solid product was washed

with cold benzene, and the insoluble residue crystallised from chloroform, preferably with the addition of light petroleum; white flakes were obtained, m. p. 189—190° (decomp.) (yield 1 g. or 23%) : 0·2048 gave 0·1268 AgCl, Cl = 15·3. $C_{19}H_{18}O_2TeCl_2$ requires Cl = 14·9%).

This dichloride dissolved sparingly in cold organic solvents excepting acetone, in which it was moderately soluble.

Reduction with aqueous metabisulphite occurred very slowly owing to the sparing solubility of the dichloride. After 6 hours, a bright yellow powder remained, which on repeated crystallisation from dilute alcohol formed yellow needles softening at 123° and melting at 128° : 0·0961 gave 0·1976 CO_2 and 0·0390 H_2O, C = 56·08, H = 4·51. $C_{19}H_{18}O_2Te$ requires C = 56·23, H = 4·44%.

4 : 4-*Dibenzylcyclotelluropentane*-3 : 5-*dione* (IV) dissolved in benzene, but not in water or aqueous caustic alkalis, thus showing no residual acidity; it was quite stable to the boiling alkali.

Tellurium tetrachloride did not condense in chloroform with 3 : 3-di-*p*-nitrobenzylacetylacetone (Mech, *Compt. rend.*, 1906, **143**, 753; 1908, **146**, 1410), and it was not found possible by varying the experimental conditions to prepare 3-*p*-nitrobenzylacetylacetone. Sodium acetylacetone did not interact with *p*-nitrochlorobenzene after prolonged boiling in alcoholic solution.

Diisobutyrylmethane, $CH_2[CO \cdot CH(CH_3)_2]_2$.

Although both di-*n*-butyrylmethane and *n*-butyryl*iso*butyrylmethane are known, the di*iso*-compound has not hitherto been described. It was prepared through its highly characteristic copper salt as follows : A mixture of 20 g. of methyl *iso*propyl ketone, 80 g. of ethyl *iso*butyrate, and 5·7 g. of sodium was kept at 0° for several hours, then allowed to attain the laboratory temperature. After 2 days, the mixture was poured on to crushed ice, the aqueous layer separated quickly, washed with ether, acidified, and treated with cupric acetate, when a bluish-green precipitate was obtained.

The ester layer was shaken with a large bulk of water, the aqueous portion separated, washed with ether, and run into aqueous cupric acetate containing acetic acid, when dark blue copper di*iso*butyrylmethane separated (5·6 g.). The foregoing bluish-green precipitate was extracted with petroleum (b. p. 40—60°), when green copper *iso*butyrate remained undissolved whilst the petroleum extract yielded another crop of the dark blue copper diketone.

When crystallised repeatedly from petroleum (b. p. 40—60°), *copper diisobutyrylmethane* was obtained in large, intensely blue rhombohedra; each crystal was a perfect parallelepiped showing

no facets, m. p. 113—114° : 0·6740 gave 0·1432 CuO, Cu = 16·79; 0·1154 gave 0·2442 CO$_2$ and 0·0850 H$_2$O, C = 57·7, H = 8·19. C$_{18}$H$_{31}$O$_4$Cu requires Cu = 17·02, C = 57·83, H = 8·03%.

This copper salt was very soluble in cold organic solvents, giving bluish-green solutions. In hot benzene, it dissolved so readily that even in thin layers the liquid was opaque. The free ketone, isolated from its copper derivative (15 g.) by dilute sulphuric acid in presence of ether, was obtained from the ethereal extract as a colourless, mobile liquid, b. p. 75—77°/7 mm. (yield 10 g.). It was miscible with organic media and its alcoholic solution developed a bright red ferric coloration.

Diisobutyrylmethane and Tellurium Tetrachloride.—A yellow solution resulted on mixing 6 g. of the diketone, 5·5 g. of tellurium tetrachloride, and 30 c.c. of chloroform, and on heating under reflux the colour changed through red to black; a considerable amount of hydrogen chloride was evolved and tellurium (1·9 g.) was deposited. After 2 hours, the light brown filtrate was concentrated in a vacuum desiccator, more tellurium being deposited (0·3 g.); the oily residue was extracted with light petroleum, and the yellow solution deposited hard, colourless, compact, tabular crystals (0·03 g.), m. p. 87—89° (decomp.), and left a residue of unchanged diketone. Qualitative analysis showed the presence of tellurium and chloride. The compound was not reducible to a yellow telluro-derivative, hence was not a *cyclo*telluripentanedione dichloride; it developed no ferric chloride coloration and was accordingly neither a telluritrichloro-derivative,

$$(CH_3)_2CH·C(OH)\!:\!CH·CO·C(CH_3)_2·TeCl_3,$$

nor a telluridichloro-compound,

$$\{(CH_3)_2·CH·CO·CH\!:\!C(OH)·C(CH_3)_2\}_2TeCl_2.$$
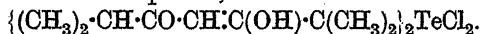
On decomposition with aqueous alkali the compound developed the earthy odour characteristic of *O*-ethyl β-diketones. Hence by exclusion the product of the condensation was probably *tellurium O-ethyldiisobutyrylmethane trichloride* (V). But owing to the very small yield the further study of the compound was not pursued.

Higher n-*Acylacetones and Tellurium Tetrachloride.*

For the two higher β-diketones employed in this section we are indebted to Mr. E. Holmes (*J. Soc. Chem. Ind.*, 1925, **44**, 108T).

1. *n*-Octoylacetone, a colourless, mobile liquid with the odour characteristic of β-diketones, boiled at 249°/755 mm. or at 117—118°/5 mm.

2-n-*Hexylcyclotelluripentane*-3 : 5-*dione* 1 : 1-*Dichloride* (VI).—The orange-red solution of 8 g. of *n*-octoylacetone and 5·9 g. of tellurium tetrachloride in 20 c.c. of dry chloroform soon blackened on heating,

but only 0·3 g. of tellurium was deposited in 4 hours. The dark brown filtrate was concentrated at the ordinary temperature and freed from unchanged diketone by repeated extraction with light petroleum, the residue concentrated further, and cooled in the ice chest. After 3 weeks, crystallisation set in. The product (1·5 g.) was stirred with carbon tetrachloride and washed with light petroleum. The carbon tetrachloride extract gave a further 0·5 g. of the dichloride (total yield 25%). The crude material was dissolved in warm benzene, filtered from tellurium, and the filtrate diluted with n-hexane, when colourless, glistening flakes separated, m. p. 80° : 0·1577 gave 0·1194 AgCl, Cl = 18·70. $C_{11}H_{18}O_2Cl_2Te$ requires Cl = 18·66%.

The dichloride was readily soluble in alcohol, chloroform, or benzene, less soluble in carbon tetrachloride, and sparingly soluble in petroleum or water.

2-n-*Hexylcyclotelluropentane*-3 : 5-*dione* (VII), produced by reduction of the preceding dichloride with cold aqueous potassium metabisulphite, was crystallised from dilute alcohol and separated in bright yellow scales, m. p. 74—75°. It dissolved readily in organic solvents, but only sparingly in water. It possessed residual acidity, dissolving in cold aqueous caustic soda, but gave no ferric coloration : 0·0969 gave 0·1510 CO_2 and 0·0540 H_2O, C = 42·50, H = 6·10; 0·2060 gave 0·0836 Te, Te = 40·59. $C_{11}H_{18}O_2Te$ requires C = 42·65, H = 5·84, Te = 41·19%.

2. *n*-Nonoylacetone, liberated from its copper salt, was a colourless, mobile liquid boiling at 140°/3 mm. On cooling in ice, it solidified to a crystalline mass, m. p. 24°, miscible with ordinary organic solvents including petroleum.

2-n-*Heptylcyclotelluripentane*-3 : 5-*dione* 1 : 1-*Dichloride* (VI).— The yellow mixture of 9 g. of *n*-nonoylacetone, 8 g. of tellurium tetrachloride, and 30 c.c. of pure dry chloroform was heated for 3 hours, filtered from 0·4 g. of tellurium, and concentrated in a vacuum desiccator. After several days, crystallisation began and 3 g. of grey product were obtained. Purified by adding petroleum (b. p. 40—60°) to its chloroform solution, the dichloride separated in colourless plates, m. p. 89° : 0·2020 gave 0·1458 AgCl, Cl = 17·85; $C_{12}H_{20}O_2Cl_2Te$ requires Cl = 17·98%.

2-n-*Heptylcyclotelluropentane*-3 : 5-*dione* (VII), prepared by the bisulphite reduction of the foregoing dichloride, separated from hot dilute alcohol in bright yellow, woolly masses, m. p. 89° : 0·1105 gave 0·1829 CO_2 and 0·0638 H_2O, C = 45·14, H = 6·61; 0·2620 gave 0·1020 Te, Te = 38·94. $C_{12}H_{20}O_2Te$ requires C = 44·52, H = 6·18, Te = 39·41%.

This telluro-derivative was only sparingly soluble in water, but

exhibited residual acidity by dissolving more readily in dilute aqueous caustic soda to a solution depositing tellurium on boiling.

Tellurium n-Nonoylacetone Trichloride.—Tellurium tetrachloride (4 g.) was mixed with 4·5 g. of nonoylacetone in chloroform solution and refluxed for 2½ hours. After concentrating the clear solution in a vacuum desiccator for 48 hours, the solid which separated was freed from tarry matter by washing successively with carbon tetrachloride and petroleum (b. p. 40—69°) and crystallised by dissolving in warm chloroform with the addition of light petroleum, when colourless, glistening flakes were obtained, m. p. 114—115° with blackening (yield 1 g.). Its chloroform–alcohol solution instantly developed a ferric coloration : 0·1557 gave 0·1555 AgCl, Cl = 24·70. $C_{12}H_{21}O_2Cl_3Te$ requires Cl = 24·71%.

Tellurium *n*-nonoylacetone trichloride was slowly decomposed by moisture, liberating the diketone and depositing tellurium dioxide; its ether–chloroform solution gave with aqueous cupric acetate a pale green precipitate of a copper salt. When boiled with chloroform, it did not evolve hydrogen chloride, but was decomposed on treatment with aqueous metabisulphite.

From the mother-liquors of the foregoing trichloride 0·5 g. of the cyclic dichloride was subsequently isolated.

CXIV.—*The Interaction of Hydrogen and Carbon Dioxide on the Surface of Platinum.*

By CHARLES ROSS PRICHARD and CYRIL NORMAN HINSHELWOOD.

HYDROGEN and carbon monoxide are known to form adsorbed layers on the surface of platinum which are stable at quite high temperatures, and which largely determine the mechanism of catalytic reactions undergone by these gases in contact with the metal. Little is known about the adsorption of carbon dioxide. The kinetics of the reaction $H_2 + CO_2 = H_2O + CO$ on the surface of a heated platinum wire present points of interest in connexion with the relative adsorptions of the various gases. The interaction of carbon dioxide and hydrogen has been investigated from 870° to 1122°, over which range the change proceeds at a con-

veniently measurable rate.   It was made irreversible by the absorp-
tion of the water formed, and was shown to go to completion,
analysis proving the product to consist entirely of carbon mon-
oxide.   No hydrocarbons are formed under these conditions.

The apparatus consisted of a cylindrical bulb with an axial
electrically heated platinum wire, the temperature of which was
known from its resistance, and could be controlled so that reaction
velocities were reproducible to 1%.   The bottom of the vessel
contained concentrated sulphuric acid to absorb water, and the
apparatus was kept in ice during the experiments.   The rate of
reaction was found by changes in pressure exactly as described for
the catalytic decomposition of nitrous oxide (this vol., p. 327).
The actual reaction bulb is shown in Fig. 1.

The continuous and accurate control of the energy supplied to
the wire was even more important than in the nitrous oxide experi-
ments owing to the rapidly chang-
ing thermal conductivity of the
gas mixture.   It presented no
difficulty, however.   Provided
that the wire was heated to 1000°
in a high vacuum between the
experiments, satisfactorily repro-
ducible results were obtained.
The hydrogen was electrolytic,
passed over heated platinum to
remove oxygen; carbon dioxide
was obtained from magnesite.

FIG. 1.

Both gases were dried with phosphorus pentoxide.   Nearly 200
separate fillings were made.   In many cases complete reaction–time
curves were plotted, but always the amount of change after at least
two fixed periods of time was noted.

Most of the experiments were made at 1000°.   The results were
as follows.   Each statement is based upon several complete series
of experiments.

1. When the pressure of carbon dioxide is kept constant, the
rate of formation of carbon monoxide increases almost linearly
with the pressure of hydrogen, at least up to 300 mm.   This is
shown in curves I and II of Fig. 2.

2. When the pressure of hydrogen is kept constant, the rate of
reaction is at first proportional to the pressure of carbon dioxide,
and then passes through a maximum when the pressure of carbon
dioxide is about double that of the hydrogen.   Larger pressures
of carbon dioxide have a great retarding influence, although it is
remarkable that the sharpness of the maximum seems to vary
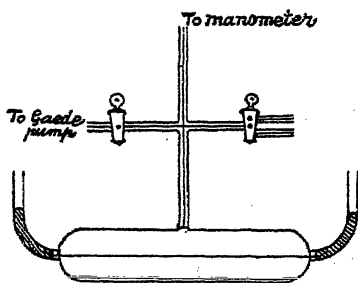
with the state of the wire. These points are illustrated by the curves in Fig. 3.

3. Carbon monoxide has a slight retarding influence, but considerably less than might have been expected (curve III, Fig. 2).

4. When the reacting gases are in equimolecular proportions (the pressure of each being 100 mm.), the course of the reaction is very nearly unimolecular, the time required for three-quarters of the reaction to complete itself being double that for half. But

FIG. 2.

Pressure of hydrogen or carbon monoxide.
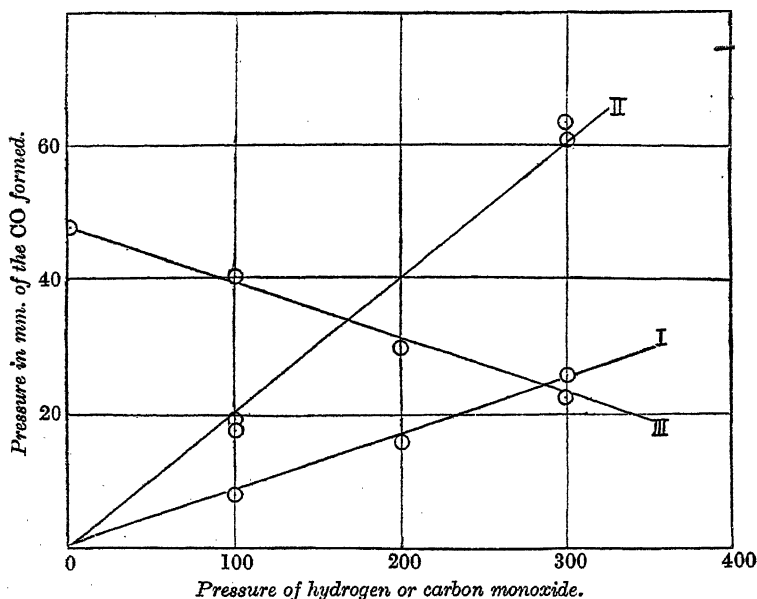
I 870°; 100 mm. carbon dioxide in each instance. Abscissae represent varying H_2 pressures, ordinates give the pressure in mm. of the CO formed in 1,200 seconds; II 1000°, 300 seconds, otherwise as I. III 100 mm. H_2; 100 mm. CO_2. Abscissae show pressure of added CO; ordinates, the reaction in 300 seconds. 1000°.

the previous results show that this is to some extent a coincidence. A typical experiment illustrating the course of the reaction is given below, t being the time in seconds and x being the pressure in mm. of the carbon monoxide formed.

Temp. 1050°; pressure of $H_2 = 100$ mm.; pressure of $CO_2 = 100$ mm.

120	300	400	600	800	1000	1200	1400	1800	∞
16	30	37·5	51	61	68·5	75	79·5	85	99

The influence of the pressures of the various gases is shown in the curves. The employment of the amount of change in 120

or 300 seconds as a measure of the rate of reaction is justified by the small deviation only of the reaction–time curves from linearity in their initial stages.   Other methods of presenting the results give curves exactly like those in the figures.   To ensure that the results were not influenced by any drift in catalytic activity, the experiments of a given series were made in a random order, and after each two or three a control experiment was made at some standard pressure to ascertain that the wire had not changed.

FIG. 3.

Pressure of carbon dioxide (mm. of Hg).
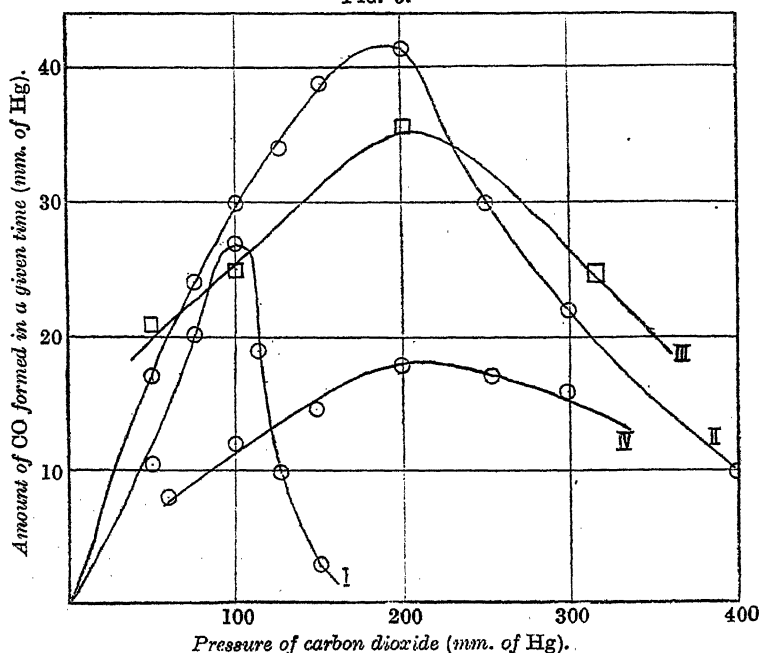
I 50 mm. H$_2$; 1000°; 300 seconds.   II 100 mm. H$_2$; 1000°; 300 seconds.
III 100 mm. H$_2$; 1120°; 120 seconds.   IV 100 mm. H$_2$; 1000°; 120 seconds.
State of wire different in II and IV.

For example, in the series shown in Fig. 3, curve II, two experiments with carbon dioxide and hydrogen each at 100 mm. pressure showed the percentage formation of carbon monoxide to be 17 and 17·5 after 120 seconds and 30 and 30 after 300 seconds, six experiments intervening.

Since the rate of reaction is dependent on the adsorption of three different gases, the influence of temperature is so complex as to be of little interest at present.   An empirical temperature coefficient was, however, determined.   For 100 mm. of hydrogen and 100 mm. of carbon dioxide the initial rate of reaction increases

2·85 times for 100° over the range 900° to 1100°. This gives an apparent heat of activation of approximately 33,000 calories.

Perhaps the most remarkable result is the apparent strong adsorption of carbon dioxide shown by its poisoning effect at higher pressures. At lower temperatures carbon dioxide is not much adsorbed by platinum, and experiments specially made on the relative adsorption of hydrogen and carbon dioxide by platinised asbestos at 970° showed strong adsorption of hydrogen, that of carbon dioxide being negligible in comparison, and indeed indistinguishable from the adsorption, if any, of the nitrogen used for calibrating the apparatus. We must therefore assume that the catalytic activity of the surface is localised in certain active points forming a small fraction only of the total surface.

A simple mechanism which now accounts for most of the facts is that reaction occurs when hydrogen and carbon dioxide become adsorbed adjacent to each other on an active part of the surface. It must be assumed further that the fraction of the active surface covered by carbon dioxide increases from zero to nearly unity as the pressure of carbon dioxide increases from 0 to 400 mm., whilst the adsorption of hydrogen on those points left free from carbon dioxide is never very great, so that we have to deal with that portion of the hydrogen adsorption isotherm where adsorption is more or less directly proportional to pressure. (It is true that saturation, although not reached in the experiments, would be reached at pressures considerably higher than 300 mm.) We then obtain the equation $d[CO]/dt = k[H_2]\sigma(1 - \sigma)$, where σ is the fraction of the active surface covered with carbon dioxide. This gives the linear dependence on hydrogen pressure over the range of pressures used in the experiments, and the maximum in the rate of reaction with increase of carbon dioxide pressure.

It is remarkable that there does not appear to be a simple competition between the hydrogen and carbon dioxide for the active surface, the hydrogen occupying all the active points left unoccupied by carbon dioxide. If this were so, the velocity would not vary linearly with the hydrogen pressure over so large a range, and the hydrogen curves would resemble the carbon dioxide curves. The results throw an interesting light on the adsorptive capacity of the surface, since it appears that the relative adsorbability of hydrogen and carbon dioxide on the active points bears no relation to that on the total surface. Moreover, unpublished experiments of Burk and Hinshelwood have shown that even at these high temperatures the decomposition of ammonia on platinum is retarded by hydrogen in a way which shows that even at 100 mm. the hydrogen covers quite a large fraction of the surface which

is active in causing the decomposition of ammonia. We have also found that carbon dioxide at a pressure of 400 mm. has only a slight retarding effect on the decomposition of nitrous oxide on platinum—the same wire as that used in the present series of experiments—confirming the conclusion that the points on which the carbon dioxide is adsorbed constitute only a small fraction of the surface.

CXV.—*Asymmetric Compounds of Quinquevalent Arsenic.*

By JOHN ALFRED AESCHLIMANN.

ATTEMPTS to resolve quaternary arsonium compounds by means of camphor- or bromocamphor-sulphonic acid have been made by Michaelis (*Annalen*, 1902, **321**, 158), Winmill (J., 1912, **101**, 720), and Burrows and Turner (J., 1921, **119**, 426), but in no case were two forms of the salt isolated.

Compounds of the type abcAs:O have now been investigated in which one of the groups a, b, and c contains an acidic radical for combination with an active base in order to effect the resolution. It was hoped that the removal of the active group would have less tendency to alter the spatial arrangement of the groups round the central atom than is the case when the active group is attached to the arsenic atom as in the older method (compare Kipping, J., 1910, **97**, 755; Jones, *Proc. Camb. Phil. Soc.*, 1904, **12**, 489; Meisenheimer, *Ber.*, 1924, **57**, 1744); and that racemisation might thus be prevented.

No evidence of resolution was obtained, however, in the case of *oo'*-dicarboxydiphenylarsinic anhydride (Aeschlimann and McCleland, J., 1924, **125**, 2025), or o-*carboxydiphenylmethylarsine oxide* (I). Phenyl-α-naphthylmethylarsine oxide, the resolution of which was attempted by Burrows and Turner (*loc. cit.*), yielded a crystalline sulphonic acid on sulphonation. The brucine and quinine salts of the acid were amorphous and the various fractions into which the crystalline strychnine salt was separated all gave rise to an inactive ammonium salt. *l*-Phenylethylamine also failed to effect resolution.

o-*Carboxydiphenylmethylarsine*, the production of which from

F F*

o-carboxyphenylmethylchloroarsine and benzene by the Friedel-Crafts reaction is unsatisfactory (compare Burrows and Turner, *loc. cit.*, p. 430), is readily obtained by the interaction of magnesium phenyl bromide and *o*-carboxyphenylmethylarsinous anhydride (Aeschlimann and McCleland, *loc. cit.*, p. 2033). This reaction may prove to be of value for the preparation of arsines containing a carboxyl group, the only method hitherto available being the oxidation of tolylarsines (Michaelis, *loc. cit.*) and reduction of the oxide produced.

(I.)   (II.)   (III.)
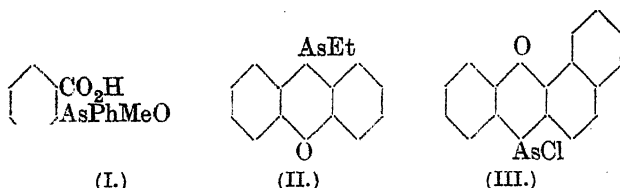
10-Ethylphenoxarsine (II), which has been obtained as a colourless oil (contrast Lewis, Lowry, and Bergheim, *J. Amer. Chem. Soc.*, 1921, **43**, 891, where a compound, m. p. 218°, is named 6-ethylphenoxarsine), combines readily with alkyl iodides and with bromoacetic acid to form stable, crystalline, quaternary salts which it is hoped to examine further. The addition compound with bromoacetic acid produces brucine hydrobromide when it is treated with brucine, as does also carboxymethylphenyl-α-naphthylmethylarsonium bromide, and the resulting glassy betaine does not combine further with brucine.

10-Ethylphenoxarsine can be oxidised to a water-soluble arsine oxide, which forms a hydrate. Either the arsine or its oxide can be sulphonated and the sulphonic acid produced gives alkaloid salts which are very soluble in water.

Phenyl α-naphthyl ether condenses with arsenious chloride in presence of aluminium chloride to produce 7-*chloro*-αβ-*naphthaphenoxarsine* (III).

EXPERIMENTAL.

oo′-Dicarboxydiphenylarsinic anhydride (Aeschlimann and McCleland, *loc. cit.*), crystallised from hot water, was kept over sulphuric acid for 4 weeks, until its weight had become constant (Found : loss = 5·2. $C_{14}H_9O_5As,H_2O$ requires $H_2O = 5·1\%$). The anhydride ring, therefore, is not very stable.

The hygroscopic quinine salt, the brucine salt, and the phenylethylamine salt each gave an inactive acid after removal of the base.

o-Carboxydiphenylmethylarsine.—Magnesium phenyl bromide (prepared from 30 g. of bromobenzene in ether) was added to 42 g. of *o*-carboxyphenylmethylarsinous anhydride in benzene during 30 minutes, and the mixture heated for 4 hours. After removal

of the solvent, the residue was treated with dilute acid, the aqueous layer removed, and the pasty residue crystallised from alcohol (yield 20 g.); m. p. 168°. Unchanged anhydride was recovered from the mother-liquor (Found : C = 57·8; H = 4·5; As, by direct titration with iodine, = 26·7. $C_{14}H_{13}O_2As$ requires C = 58·3; H = 4·5; As = 26·1%).

o-*Carboxydiphenylmethylarsine Oxide* (I).—The preceding arsine in warm alcoholic solution was oxidised with hydrogen peroxide. The product crystallised from alcohol or acetic acid in colourless needles, m. p. 242° (Found : C = 55·4; H = 4·3. $C_{14}H_{13}O_3As$ requires C = 55·3; H = 4·3%). If the crude arsine is used for the preparation of the oxide, o-carboxyphenylmethylarsinic acid remains in the aqueous alcoholic solution.

Alkaloid salts were obtained neither from the acid (I) in alcoholic solution nor from its sodium salt and alkaloid hydrochloride. The *l*-phenylethylamine salt, obtained by using an excess of the base in aqueous solution, appeared to decompose on heating with water. It was separated into three fractions by crystallisation from warm water, but the arsine oxide recovered from them was inactive.

The brucine salt (5 g.) of o-carboxydiphenylmethylarsine, on oxidation with hydrogen peroxide, gave 2·2 g. of the preceding arsine oxide, complete decomposition of the salt therefore having taken place.

Sulphophenyl-α-naphthylmethylarsine Oxide.—A solution of 10 g. of phenyl-α-naphthylmethylarsine oxide (prepared by oxidising the arsine [Burrows and Turner, *loc. cit.*] with hydrogen peroxide in acetone or alcohol and recrystallising the product from toluene) in 20 c.c. of oleum (20% SO_3) was allowed to cool and poured into water. The precipitate was dissolved in aqueous ammonia, and the solution boiled with charcoal and filtered into hot acetic acid, the *sulphonic acid* separating, on cooling, in fine, white crystals, m. p. 249°. Mr. E. S. Dewing, who kindly examined the crystals, reports that they show straight extinction and have a habit similar to that of baryta with two planes of symmetry; the existence of enantiomorphous forms would therefore appear to be impossible (Found : C = 52·1; H = 3·9; S = 8·15. $C_{17}H_{15}O_4SAs$ requires C = 52·4; H = 3·9; S = 8·2%).

The *addition compound* obtained by heating phenyl-α-naphthylmethylarsine and bromoacetic acid on the water-bath for 1 hour crystallised from alcohol to which hydrobromic acid had been added. It melted at 145—150° (decomp.), but was not quite pure (Found : Br = 18·55. $C_{19}H_{17}O_2BrAs$ requires Br = 18·45%).

10-*Ethylphenoxarsine* (II).—A warm solution of 10-chlorophenoxarsine (64 g.) in 200 c.c. of benzene was added to the Grignard re-

agent prepared from 23 c.c. (excess) of ethyl bromide and 7 g. of magnesium. The mixture was heated for 4 hours, decomposed in the usual manner, and the solution dried and distilled in a vacuum; the phenoxarsine (yield 42 g.) passed over at 194°/20 mm., leaving a small quantity of the chlorophenoxarsine. A colourless liquid free from chlorophenoxarsine was obtained by refractionation in a vacuum, but it did not crystallise (Found : C = 61·8; H = 4·8. $C_{14}H_{13}OAs$ requires C = 61·8; H = 4·8%).

10-*Ethylphenoxarsine oxide*, m. p. 99°, was obtained by evaporating a solution of the phenoxarsine in hydrogen peroxide, and crystallised from hot benzene. It contained a molecule of water, which it lost below 60° in a vacuum and regained in the air (Found : C = 54·1; H = 4·9; loss = 5·6%. $C_{14}H_{13}O_2As,H_2O$ requires C = 54·9; H = 4·9; H_2O = 5·8%).

Sulpho-10-*ethylphenoxarsine oxide* was obtained by sulphonating the oxide under similar conditions to those described above, but the mixture was heated at 100°. The acid was soluble in hot water and insoluble in alcohol. It changed in appearance at 250° without charring, but did not melt below 300° (Found : C = 45·4; H = 3·5; equiv. = 368. $C_{14}H_{13}O_5SAs$ requires C = 45·6; H = 3·5%; equiv. = 368).

10-*Methyl*-10-*ethylphenoxarsonium iodide*, formed when equivalent quantities of 10-ethylphenoxarsine and methyl iodide were heated for 4 hours at 50°, crystallised from hot alcohol in compact, white crystals, m. p. 186° or 193° according to the rate of heating (Found : C = 43·1; H = 4·0; I = 30·6. $C_{15}H_{16}OIAs$ requires C = 43·5; H = 3·9; I = 30·7%). An orange-red compound, probably an isomeride, also was obtained.

10 - *Methyl* - 10 - *ethylphenoxarsonium* d - *bromocamphorsulphonate*, m. p. 153°, obtained by treating the white iodide with silver d-bromocamphorsulphonate in alcohol, could be crystallised from alcohol or water. Various fractions of the salt had $[M]_{5461} + 339°$ in 1·5% aqueous solution and + 398° in 5% alcoholic solution (compare Winmill, *loc. cit.*) (Found : C = 50·0; H = 5·0. $C_{25}H_{30}O_5BrSAs$ requires C = 50·2; H = 5·0%).

10 : 10-*Diethylphenoxarsonium iodide* crystallises in pale straw-coloured needles, m. p. 193° (Found : C = 45·1; H = 4·3. $C_{16}H_{18}OIAs$ requires C = 44·8; H = 4·2%).

10-*Carboxymethyl*-10-*ethylphenoxarsonium bromide* was obtained by heating 10-ethylphenoxarsine with bromoacetic acid for 10 minutes at 100°, and was sufficiently stable to be recrystallised from hot alcohol (Found : Br = 19·6; equiv. = 412. $C_{16}H_{16}O_3BrAs$ requires Br = 19·5%; equiv. = 411).

7-*Chloro*-αβ-*naphthaphenoxarsine* (III), m. p. 168°, was obtained

by heating a mixture of arsenious chloride, phenyl α-naphthyl ether, and aluminium chloride from 180° to 250°, distilling in a vacuum, and recrystallising from benzene the fraction obtained between 210° and 240°/20 mm. The yield was small and was not improved by various modifications (Found : C = 58·9; H = 2·95. $C_{16}H_{10}OClAs$ requires C = 58·6; H = 3·05%).

Resolution of r-*Phenylethylamine.*—A solution of the base and the equivalent quantity of tartaric acid in boiling alcohol (15 parts) was cooled to 60°, stirred for 24 hours, and the mother-liquor poured off from the heavy, crystalline precipitate of *l*-base *d*-tartrate. The liquor set to a paste of hair-like needles on cooling, but the pure *d*-base could not be obtained from these after repeated crystallisation as described by Betti (*Gazzetta*, 1920, **50**, 276). The impure base liberated from the salt was converted into the *l*-malate in aqueous solution by Loven's method (*J. pr. Chem.*, 1905, **72**, 307), a moderately pure salt of the *d*-base being obtained. The salts of the *d*- and the *l*-base were crystallised once from a little water. The *d*-base *l*-malate gave α + 0·05° (*l* = 2) in 5% aqueous solution, whereas a specimen prepared wholly by Loven's method gave α − 0·1° after four crystallisations. The *l*-base *d*-tartrate gave α + 1·04° (*l* = 2) in 4% aqueous solution.

The *l*-base liberated from the tartrate had at 18° $[\alpha]_{5161}$ − 48·2°, $[\alpha]_{5790}$ − 42·4°; $[\alpha]_{5461}$ − 55·3° and $[\alpha]_{5790}$ − 49·6° in 1·8% benzene solution; and $[\alpha]_{5461}$ − 34·4° and − 26·9° in 1·5% solution in 50% and 20% aqueous alcohol, respectively.*

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CXVI.—*The Chemistry of the Three-carbon System. Part IV. A Case of Retarded Mobility.*

By GEORGE ARMAND ROBERT KON and REGINALD PATRICK LINSTEAD.

THE cases of tautomerism considered in Part III. (this vol., p. 616) fall into a category exhibiting but a small degree of mobility, whilst those formerly described belonged essentially to a group possessing a very mobile tautomeric system. Thus *cyclo*hexenyl-acetone prepared by the Blaise-Maire reaction from the chloride

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* The above values agree with those of Loven for the free base (40·16° for the D line) and of Kipping and Hunter (J., 1903, **83**, 1149), who obtained the value −25° in aqueous solution clarified by alcohol. The values have not hitherto been correlated, the resolutions having been carried out by different methods.

of *cyclo*hexylideneacetic acid (I) was identical with the ketone derived from the chloride of Δ^1-*cyclo*hexenylacetic acid (II) :

$$(\text{I.}) \quad CH_2 \Big\langle {}^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2} \Big\rangle C{:}CH{\cdot}CO_2H \longrightarrow$$

$$CH_2 \Big\langle {}^{CH_2 \cdot CH_2}_{CH_2-CH} \Big\rangle C{\cdot}CH_2{\cdot}COMe \longleftarrow CH_2 \Big\langle {}^{CH_2 \cdot CH_2}_{CH_2-CH} \Big\rangle C{\cdot}CH_2{\cdot}CO_2H \,(\text{II.})$$
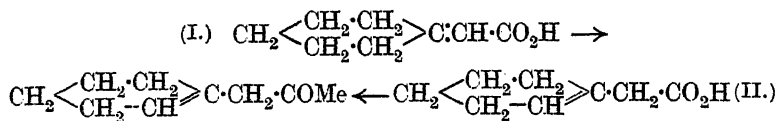
The conditions under which the synthesis was carried out precluded the possibility of previous isomerisation on the part of the acid chloride used. The same ketone is also obtained by condensation of *cyclo*hexanone with acetone and by the distillation of calcium *cyclo*hexanediacetate. It follows, therefore, that, whichever form is first produced in these reactions, the double linking assumes the stable position so rapidly that one and the same substance—or equilibrium mixture of constant composition and properties—is isolated. We wish to emphasise that the equilibrium between the two forms of *cyclo*hexenylacetone is established, apparently, in the absence of a reagent and is not dependent on the presence of, say, sodium ethoxide as suggested by Farmer (J., 1923, **123**, 3324), although his remarks apply to a number of other cases studied by us.

There is, however, no reason why the mobility of a three-carbon system should not be reduced (by substitution, etc.) to such an extent that the above condition is realised. The substance would then be capable of isolation in two distinct forms—an $\alpha\beta$ and a $\beta\gamma$—but these would be converted one into the other in the presence of a mild reagent or form an equilibrium mixture similar to those observed in cases of keto-enol tautomerism. Certain substances will now be described which satisfy this condition and are particularly interesting because they occupy as it were the border line between the two classes of tautomeric substances—they display retarded mobility.

When the chlorides of the two acids IV and VI (see Part III, *loc. cit.*) are treated with zinc methyl iodide, they give rise to the ketones V and VII, the latter being identical with that produced by the distillation of calcium $\beta\beta$-diethylglutarate (Kon, J., 1921, **119**, 810).

$$(\text{IV.}) \quad {}^{Et}_{Et}{\big>}C{:}CH{\cdot}CO_2H \longrightarrow {}^{Et}_{Et}{\big>}C{:}CH{\cdot}COMe \quad (\text{V.})$$

$$(\text{VI.}) \quad {}^{Et}_{Me \cdot CH}{\big>}C{\cdot}CH_2{\cdot}CO_2H \longrightarrow {}^{Et}_{Me \cdot CH}{\big>}C{\cdot}CH_2{\cdot}COMe \quad (\text{VII.})$$
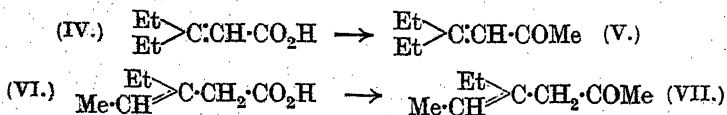
The two ketones are quite distinct, giving different semicarbazones and yielding different oxidation products in accordance with the constitutions assigned to them ; (V) also shows the expected

exaltation of the molecular refraction. The two compounds are, therefore, non-tautomeric under the conditions of the Blaise-Maire synthesis, in striking contrast to the case of *cyclo*hexenylacetone. In presence of sodium ethoxide, however, the three-carbon system in these compounds becomes more mobile and the ketone (VII) condenses with ethyl sodiomalonate just as readily as its isomeride, giving the ester (VIII), which passes on hydrolysis into the beautifully crystalline 3 : 5-*diketo*-1 : 1-*diethyl*cyclo*hexane* (IX).

(VIII.) $\dfrac{Et}{Et}{>}C{<}\dfrac{CH_2\text{———}CO}{CH(CO_2Et)\cdot CO}{>}CH_2 \rightarrow \dfrac{Et}{Et}{>}C{<}\dfrac{CH_2\cdot CO}{CH_2\cdot CO}{>}CH_2$ (IX.)
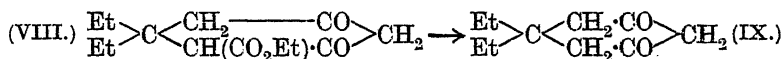
It is obvious that an equilibrium must first be established between the two forms and as the $\alpha\beta$-form reacts more of it is produced until the reaction is complete.

This equilibrium is established slowly in the absence of a reagent with which the $\alpha\beta$-form can combine; thus, for instance, only 15% conversion can be detected in 24 hours in the presence of sodium ethoxide alone. The converse change, however, is more rapid, some 30% of the $\beta\gamma$-form being produced from the $\alpha\beta$ under the same conditions. The study of this change is considerably complicated by the fact that the semicarbazones of the two ketones, which should afford a ready means of separation, form eutectic mixtures which cannot be separated into their components without great difficulty. One such eutectic, containing about 80% of the $\alpha\beta$-form, has a definite crystalline form, melts at 121—122°, and has been prepared synthetically by crystallising a suitable mixture of the two components. The result of the above experiments shows clearly, however, that the $\beta\gamma$-form of the ketone is the more stable and it may be mentioned that the $\alpha\beta$-form is apparently quantitatively converted into the $\beta\gamma$ by the action of dilute sulphuric acid; the change appears to be irreversible. The effect on the $\beta\gamma$-form of the addition and subsequent elimination of hydrogen bromide leads to a similar conclusion, because the ketone is recovered unchanged whereas in the cases studied by Blaise (*Bull. Soc. chim.*, 1905, **33**, 43) the $\beta\gamma$-form was completely isomerised to the $\alpha\beta$ by similar treatment. Repeated attempts were made to alkylate the ketone (VII), but without success.

It appeared to be of interest to compare the ketones (V) and (VII) with the closely related *cyclo*pentenylacetone (XI) which had already been prepared by the distillation of calcium *cyclo*pentanediacetate (Kon, *loc. cit.*). On treating the chlorides of the two isomeric acids (X) and (XII) with zinc methyl iodide, one and the same ketone was obtained, identical in every respect with the substance previously prepared.

(X.) $\begin{array}{c}CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2\end{array}\!\!>\!\!C\colon\! CH \cdot CO_2H$ $\begin{array}{c}CH_2 \cdot CH_2 \\ CH_2 - CH\end{array}\!\!>\!\!C \cdot CH_2 \cdot COMe$ (XI.)

(XII.) $\begin{array}{c}CH_2 \cdot CH_2 \\ CH_2 - CH\end{array}\!\!>\!\!C \cdot CH_2 \cdot CO_2H$
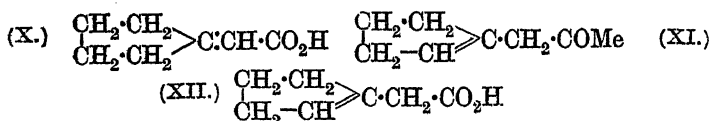
This ketone appears to possess the $\beta\gamma$-structure (XI) under ordinary conditions, but it is capable of reacting in the $\alpha\beta$-form because it condenses with ethyl sodiomalonate to give an 85% yield of the corresponding dihydroresorcinol derivative (Norris and Thorpe, J., 1921, 119, 1199). On the other hand, it readily undergoes alkylation in the same way as *cyclo*hexenylacetone, a 35% yield of an α-ethyl derivative being obtained; as a matter of fact, no unchanged *cyclo*pentenylacetone is isolated in this reaction, the by-products consisting of high-boiling oils doubtless formed as the result of internal condensation.* The ketone is thus in every way analogous to *cyclo*hexenylacetone; the three-carbon system in this substance possesses a high degree of mobility, thus differing from the otherwise very similar open-chain ketones (V) and (VII). The difference is doubtless bound up with the great tendency for a double linking to migrate towards a five- or six-membered alicyclic ring, although the precise significance of this is not yet apparent; it is hoped that the study of a number of related phenomena which is at present in progress will shed further light on the subject.

Experimental.

δ-*Ethyl*-Δ^{γ}-*hexen*-β-*one* (V).—Pure $\beta\beta$-diethylacrylyl chloride (see Part III.) was added to zinc methyl iodide in benzene, and the ketone (yield 64%) was isolated as described in Part I (J., 1923, 123, 1361). The pure ketone regenerated from the semi-carbazone boiled at 59°/14 mm., 164°/770 mm., and had $d_4^{17\cdot 9°}$ 0·85633, $n_D^{17\cdot 9°}$ 1·45223, $[R_L]_D$ 39·75 (calc. 38·72); it had a powerful odour reminiscent of that of mesityl oxide. The ketone did not give a colour with alcoholic ferric chloride.

The *semicarbazone* crystallised from ethyl acetate–petroleum in flattened needles, m. p. 159° (Found : $C = 59\cdot 3$; $H = 9\cdot 6$; $N = 23\cdot 2$. $C_9H_{17}ON_3$ requires $C = 59\cdot 0$; $H = 9\cdot 3$; $N = 22\cdot 9\%$). A semicarbazide-semicarbazone could not be obtained.

The ketone was oxidised with cold 3% potassium permanganate solution in the presence of sodium hydrogen carbonate. The diethyl ketone obtained in the neutral fraction of the oxidation product was identified by means of its *p*-nitrophenylhydrazone,

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* We were unable to introduce a methyl group into *cyclo*pentenylacetone under similar conditions; the methylated ketone was, however, prepared in small quantity by the action of magnesium methyl iodide on α-*cyclo*pentyl-idenepropionitrile (Birch and Kon, J., 1923, 123, 2440).

m. p. 137°, whilst oxalic acid constituted the acid fraction. Diethyl ketone was also produced by the action of ozone. The ketone (5·3 g.) was condensed with ethyl sodiomalonate under the conditions used by Norris and Thorpe (*loc. cit.*), 8·7 g. of the crude ester being obtained. This could not be induced to crystallise and was therefore hydrolysed with barium hydroxide, 3·5 g. (50%) of *diethyldihydroresorcinol* (IX) being obtained; this crystallised readily from benzene and light petroleum in flattened needles, m. p. 113° (Found : C = 71·1; H = 9·5. $C_{10}H_{16}O_2$ requires C = 71·4; H = 9·6%).

δ-*Ethyl*-Δ$^\delta$-*hexen*-β-*one* (VII).—This substance was prepared (yield 68%) in exactly the same way as its αβ-isomeride, using the chloride of β-ethyl-Δ$^\beta$-pentenoic acid. It was isolated in the form of its semicarbazone, m. p. 144—145° after purification; this proved to be identical with the semicarbazone previously obtained by Kon (*loc. cit.*). The ketone regenerated from it had b. p. 57°/13 mm., 163—164°/756 mm., $d_4^{19·6°}$ 0·85883, $n_D^{19·6°}$ 1·44301, $[R_L]_D$ 38·93; it gave no colour with alcoholic ferric chloride.

The ketone, dissolved in chloroform, was treated with ozone, and the ozonide decomposed by warming with water and finally distilling in steam, when a good yield of acetaldehyde (isolated in the form of the condensation product with β-naphthol; see Part III., *loc. cit.*) was obtained; no trace of diethyl ketone could be detected in the volatile portions of the oxidation product. The residue in the flask gave an intense red colour with alcoholic ferric chloride and formed a copper compound, crystallising from alcohol in blue-grey needles, m. p. 197°, and probably consisted of propionylacetone.

The ketone was unchanged after treatment with sodium ethoxide and ethyl iodide in excess.

The condensation with ethyl sodiomalonate was carried out exactly as described for the αβ-ketone; the yield of diethyldihydroresorcinol was precisely the same (50%).

Interconversion of the αβ- *and* βγ-*Ketones.*—The pure βγ-ketone (2·5 g.) was mixed with a cold solution of 0·5 g. of sodium in 10 c.c. of alcohol and kept for 28 hours. Water was then added, the ketone isolated by means of ether and converted into the semicarbazone, which was fractionally crystallised from ethyl acetate–light petroleum (b. p. 40—60°). The first crop of crystals consisted of the βγ-semicarbazone (m. p. 138°; m. p. of mixture with pure βγ-semicarbazone 142°; with αβ-semicarbazone, 121°). The second and subsequent crops were composed of a substance forming definite needles, m. p. 121—122° (unchanged by recrystallisation). The addition of the αβ- or βγ-semicarbazone raised the melting point to 135—140°.

The same eutectic mixture of semicarbazones was prepared by mixing known quantities of the αβ- and βγ-ketones, converting the mixture into the semicarbazone, and fractionally crystallising the latter. By carefully collecting and weighing the different crops of crystals obtained, it was estimated that the eutectic mixture contains about 80% of the αβ- and 20% of the βγ-semicarbazone. From the quantity of βγ-semicarbazone and eutectic mixture obtained, the amount of isomerisation of the βγ-ketone to the αβ in the above experiment appears to be about 15%. In a simultaneous experiment carried out with the pure αβ-ketone, the amount of conversion was about 35%.

The βγ-ketone (4·2 g.) was added to 6 g. of hydrobromic acid saturated at 0°, the mixture being kept cold; after 15 minutes, it was poured into water and extracted with ether, the extract being washed, dried, and evaporated. The bromo-ketone was obtained as a heavy liquid with an odour resembling that of eucalyptus oil; it did not combine with semicarbazide. The crude substance was boiled with a solution of 5 g. of potassium hydrogen carbonate in 30 c.c. of water for about 2 hours, and the ketone was recovered in the usual way and converted into the semicarbazone. The latter proved to be the semicarbazone of the βγ-ketone accompanied by a small quantity of the eutectic mixture; it is estimated that no more than 5% conversion to the αβ-form had occurred.

The αβ-ketone (2·5 g.) was boiled with 6 c.c. of 25% sulphuric acid under reflux; the ketone was then isolated and converted into the semicarbazone. This proved to be the pure βγ-compound, the isomerisation being complete. A similar experiment was carried out with the βγ-ketone, the substance being recovered unchanged.

Δ¹-cycloPentenylacetone (XI).—Δ¹-cycloPenteneacetic acid was prepared by Wallach's method (Annalen, 1906, 347, 324) and converted into the acid chloride, b. p. 75°/23 mm. This was treated with zinc methyl iodide in the usual way, giving a 58% yield of the ketone, which was usually contaminated by an unpleasant-smelling impurity removable by repeated extraction with potassium hydroxide solution. The semicarbazone was readily obtained and could be separated into two forms, melting at 189° and 138°, respectively, and identical with the two semicarbazones obtained by Kon (loc. cit.). The ketone regenerated from the semicarbazone boiled at 69°/11 mm., 186°/765 mm., and had $d_4^{19°}$ 0·9373, $n_4^{19°}$ 1·47291, $[R_L]_D$ 36·91.

The same ketone was also obtained in 50% yield, starting with cyclopentylideneacetic acid (Harding and Haworth, J., 1910, 95, 480; compare Part III.), the chloride of which was found to

boil at 69°/13 mm. The ketone gave the two semicarbazones melting at 189° and 138° respectively, these being identical with the semicarbazones of the ketone prepared from calcium *cyclo*pentanediacetate.

No isomerisation occurred on converting either the αβ- or the βγ-acid into its chloride, because the original acid could be regenerated from it.

α-*Ethyl*-Δ¹-*cyclopentenylacetone*, $\begin{smallmatrix} CH_2 \cdot CH_2 \\ | \\ CH_2-CH \end{smallmatrix}\rangle C \cdot CHEt \cdot COMe$.—The ethylation of *cyclo*pentenylacetone was carried out exactly as in the case of the higher homologue (Part I, *loc. cit.*). A fraction boiling between 70°/16 mm. and 86°/14 mm. (mainly 84—86°/14 mm.) was obtained in 35% yield, and this did not appear to contain any unchanged original material. It reacted at once with semicarbazide acetate, giving the *semicarbazone* of the α-ethyl derivative of *cyclo*pentenylacetone; the semicarbazone was somewhat sparingly soluble in alcohol, from which it separated in colourless plates, m. p. 167° (Found : C = 63·1; H = 9·6. $C_{11}H_{19}ON_3$ requires C = 63·1; H = 9·2%).

*cyclo*Pentenylacetone could not be methylated by the action of methyl iodide and sodium methoxide, the original ketone being recovered unchanged. The α-methyl derivative was, however, prepared in small amount by the following process : α-*cyclo*Pentylidenepropionitrile (8 g.) (Birch and Kon, *loc. cit.*) was added to an excess of magnesium methyl iodide in ether. When the vigorous reaction had subsided, the mixture was warmed for an hour, the magnesium compound decomposed in the usual manner, and the volatile products distilled in steam and isolated by means of ether. They consisted of the new ketone together with a considerable amount of unchanged nitrile. The ketone was converted into its *semicarbazone*, the adhering nitrile being removed by means of light petroleum. The semicarbazone separated from dilute methyl alcohol in glistening plates, m. p. 181—182° (Found : C = 61·8; H = 9·05. $C_{10}H_{17}ON_3$ requires C = 61·5; H = 8·8%).

CXVII.—*The Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions. Part I.*

By ARTHUR JOHN ALLMAND, PERCY WALMSLEY CUNLIFFE, and ROBERT EDWIN WITTON MADDISON.

SINCE Berthollet's discovery that chlorine water is decomposed when exposed to light, with evolution of oxygen and formation of hydrochloric acid, many papers have been published on the subject. None of these, however, deals with the reaction in a systematic fashion, and the present work, carried out during 1921—1924, is an attempt to fill up some of the gaps in our knowledge of this photolysis. The literature is too voluminous to give fully here. The majority of the papers are quoted in Mellor's " Inorganic and Theoretical Chemistry," Vol. II, p. 78. Other papers dealing with the reaction are those by McLeod (*J.*, 1886, **49**, 608), Richardson and others (*Rep. Brit. Assoc.*, 1888, 89; 1889, 59; 1890, 263), Richardson (*J.*, 1891, **59**, 536), and Benrath and Schaffganz (*Z. physikal. Chem.*, 1922, **103**, 139). Little has been published on the photodecomposition of solutions of hypochlorous acid. Gay-Lussac (*Annalen*, 1842, **43**, 153) and Williamson (*ibid.*, 1855, **54**, 133) both refer to the acid as being photosensitive. Foerster and Jorre (*J. pr. Chem.*, 1899, **167**, 81) confirm this, whilst stating that the photosensitivity is small. Pedler (*J.*, 1890, **57**, 613) carried out a few experiments on the subject, Clark and Iseley (*J. Ind. Eng. Chem.*, 1920, **12**, 1116) state that its photodecomposition in sunlight is monomolecular, and finally, a few observations are recorded by Benrath and Schaffganz (*loc. cit.*).

With respect to the decomposition of chlorine water, the main results of previous work can be summarised as follows. The reaction in the dark is inappreciable (Draper). The products of the photo-reaction are generally given (more particularly in the earlier papers, though this is also the case in the quite recent work of Benrath and his pupils) as merely hydrochloric acid and oxygen. Popper (1885) was the first to notice that chloric acid can be formed in quantity. This observation was confirmed by Gore (1889), Klimenko (1889 and later), Pedler (1890), and Billitzer (1906), the formation of oxygen, according to the last author, being quite unimportant. Billitzer reports the production of perchloric acid, and Gore mentions hydrogen peroxide. According to Richardson (1891), the evolved oxygen is ozonised, but no hydrogen peroxide is produced. The presence of hydrochloric acid renders chlorine water far less sensitive (Bunsen and Roscoe and other subsequent workers), although, according to Billitzer, a *small* addition of acid acts as a positive

catalyst. The addition of other chlorides also retards the reaction, although less effectively than hydrochloric acid (Klimenko, Billitzer, Milbauer); so also do certain sulphates (Benrath and Schaffganz). Bromine acts as a positive catalyst (Milbauer). The evolution of the oxygen is subject to marked supersaturation effects (Berthollet). As will be seen, this circumstance probably accounts for the induction period and the " after effect " noted by Draper. The reaction goes more readily in violet light than in the rest of the visible spectrum (Davy). The temperature coefficient is 1·4 (Benrath and Tuchel).

De Saussure, assuming the validity of the $I \times t$ law, recommended the use of chlorine water as an actinometer liquid. According to Wittwer, the reaction is of the first order, and its rate is proportional to the intensity of the light. Bunsen and Roscoe, and, later, Billitzer, found no such relations, Billitzer saying that the reaction is autocatalytic. Finally, the actual primarily photosensitive constituent is imagined to be chlorine itself (earlier workers and Billitzer), hypochlorous acid (Pedler, Pebal, Jakowkin, Klimenko, and more particularly Dawson), and the ClO' ion (Benrath and Schaffganz).

Plan of Work.—It will be seen that, not only is there disagreement as to the mechanism of the reaction, but there are discordant statements even as to the chemical nature of the reaction products. No work has been done in monochromatic light, and the energetics of the reaction has not been touched. It is therefore to these points in particular that our attention has been directed.

The present paper is an account of our work on the reaction products and the factors affecting them. We adopted a working hypothesis which we subsequently found to have been previously developed up to a point by Jakowkin (*Z. physikal. Chem.*, 1899, 29, 621) and by Dawson (*Z. wiss. Phot.*, 1914, 14, 213). A solution of chlorine in water is, at the ordinary temperature, very considerably hydrolysed (Jakowkin, *loc. cit.*) according to the equation,

$$Cl_2 + H_2O \rightleftharpoons HClO + H^{\cdot} + Cl'.$$

All evidence goes to show that the addition of chlorides and, in particular, of hydrochloric acid, retards its photodecomposition. This follows qualitatively from the above equation if the hypochlorous acid molecule is considerably more photosensitive than the chlorine molecule. It would appear reasonable to suppose that the primary decomposition reaction in the case of hypochlorous acid would be

$$HClO \longrightarrow HCl + O$$
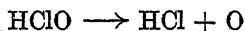
and also that oxygen atoms would be formed at an early stage when

chlorine was the photosensitive substance. (Possible reaction mechanisms will be considered more closely in the second paper). The production of molecular oxygen and chloric acid would then be due to secondary reactions, the latter substance being formed as a result of the hypochlorous acid molecules acting as acceptors for the oxygen atoms. If, therefore, by addition of suitable non-photosensitive substances, it could be arranged practically to exclude the presence from the solution during insolation of either hypochlorous acid molecules or of chlorine molecules respectively, one might expect in the first case a slow reaction with very little chlorate formation, and, in the second case, a more rapid reaction with a higher percentage of chloric acid in the product than would have been the case with ordinary chlorine water.

The addition of either hydrogen ions or chlorine ions to chlorine water will increase the chlorine concentration in the solution at the expense of that of the hypochlorous acid. Experiments were accordingly carried out with chlorine water in which the percentages of the reaction products were carefully estimated. Similar experiments were then done with chlorine dissolved in solutions of potassium chloride, lithium chloride, cadmium chloride, sulphuric acid, and hydrochloric acid of varying strengths, in order to study the effect of hydrogen ions and chlorine ions, separately and in conjunction with each other. Experiments were further done with chlorine dissolved in solutions of sodium sulphate and lithium sulphate, in order to test the effect of neutral salts, and with chlorine dissolved in bromine water and in solutions of copper sulphate, cobalt sulphate, and nickel sulphate, in connexion with later experiments on possible catalytic effects.

With the intention of affecting the Jakowkin equilibrium in favour of hypochlorous acid, experiments were carried out with chlorine water containing dissolved mercuric chloride, the idea being that, as the result of the reaction

$$HgCl_2 + 2Cl' \longrightarrow HgCl_4'',$$
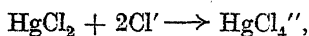
the hydrolysis of chlorine would be made almost complete. Subsequent reference to Sherrill's work (*Z. physikal. Chem.*, 1903, **43**, 734; 1904, **47**, 103) showed this not to be so, only a moderate diminution in chlorine-ion concentration being effected even by saturating the chlorine water with mercuric chloride. Measurements of Jakowkin himself led to the same conclusion.

A solution of hypochlorous acid, on insolation, immediately forms hydrochloric acid, with consequent production of chlorine in the solution. To avoid this, it is necessary to remove either the chlorine ions or the hydrogen ions as they are formed. Experiments

were done with addition of mercuric chloride to remove the chlorine ions. They were few in number, not very concordant, and are not recorded here, more particularly as, for the reason just stated, they were ill-adapted to achieve their purpose. In order to remove the hydrogen ions, the obvious course was to add to the solution the sodium salt—NaR—of a weak acid unaffected by light. The acid chosen, however, should not be so weak as to allow of the reaction

$$HClO + R' \longrightarrow ClO' + HR$$
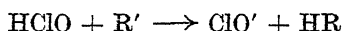
setting in, as the photosensitivity of the sodium hypochlorite formed would then complicate matters. The necessary condition is that the salt used should be of an acid with a dissociation constant which, whilst small, is appreciably greater than that of hypochlorous acid. Sodium acetate and disodium hydrogen phosphate were chosen, and the products of photodecomposition in their presence investigated. Any formation of hypochlorite ion will take place according to the respective equations

$$HClO + Ac' \longrightarrow HAc + ClO'.$$
$$HClO + HPO_4'' \longrightarrow H_2PO_4' + ClO'.$$
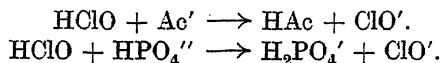
The dissociation constants K_{HAc} and $K_{H_2PO_4'}$ (Abbott and Bray, J. Amer. Chem. Soc., 1909, **31**, 729) are respectively $1·8 \times 10^{-5}$ and $1·95 \times 10^{-7}$ at 18°. The value for K_{HClO} is given as $3·7 \times 10^{-8}$ (Sand, Z. physikal. Chem., 1904, **48**, 610), $6·7 \times 10^{-10}$ (Noyes and Wilson, J. Amer. Chem. Soc., 1922, **44**, 1630), and 1×10^{-8} (Soper, J., 1924, **125**, 2227). When starting these particular experiments, we assumed the figure given by Noyes and Wilson to be probably more nearly correct than that of Sand, in which case the condition necessary for practical non-formation of hypochlorite ions would be satisfied. It would seem, however, from Soper's work, that their value is certainly too low. Adopting the figure of 1×10^{-8}, an approximate calculation shows that, in a solution containing $M/8$-$Na_2HPO_4 + M/20$-$HClO$, about 28% of the hypochlorous acid is present as hypochlorite ions, and that this proportion is reduced to about 15% when the solution is half decomposed. Our results must therefore be considered in the light of this uncertain factor. With sodium acetate, no such difficulty arises, and the production of both hydrogen- and hypochlorite-ions should be satisfactorily repressed.

<center>EXPERIMENTAL.</center>

Preparation of Solutions.—Chlorine was prepared by the action of concentrated hydrochloric acid on either potassium dichromate or potassium permanganate crystals, the gas being washed by water (in the latter case also by a solution of potassium permanganate

prior to the water washing) and then passed into distilled water or into the appropriate solution. Hypochlorous acid was prepared by the method of Bostock and Taylor (J., 1912, 101, 451), *viz.*, by distillation at a pressure of about 120—140 mm. of a mixture of bleaching powder, boric acid, and water. In some cases a solution of sodium hypochlorite was substituted for the bleaching powder. Unless the pressure were lowered well below the figure just given, the distillate was appreciably weaker, in spite of the higher hypochlorite concentration in the distilling flask. This difference is presumably due to the relative insolubility of the calcium borate resulting in the first case, and to boric acid being a weaker acid than hypochlorous acid (accepting Soper's figure for K_{HClO}). When insolating mixtures of hypochlorous acid and the above-mentioned salts, weighed quantities of the latter were dissolved in the hypochlorous acid solution.

Analytical Methods.—During the whole of the work, as will be seen later, the only decomposition products found, apart from hydrochloric acid, were chloric acid and oxygen.* In what follows, the concentrations of the different oxidising substances concerned are expressed as normalities of equivalent oxidising power. Thus " normal " solutions of chlorine, hypochlorous acid, and chloric acid contain respectively 35·5, 26·2, and 14·1 g./litre of the substance concerned. In the particular case of oxygen, supposing it to remain in solution, a normal solution would contain 8 g./litre, and it can be readily seen that, in correlating the quantity of oxygen produced during a given experiment with the corresponding loss in chlorine or hypochlorous acid, the following equation holds :

$$\text{`` Normality '' of oxygen} = 4v/22 \cdot 4V,$$

where V is the volume of the insolated solution, and v the volume of evolved oxygen at N.T.P.

Chlorine and hypochlorous acid were determined by delivering a known volume of the solution under the surface of an acidified 5% solution of potassium iodide, and titrating with $N/10$-thiosulphate. A special experiment showed that solutions containing hydrochloric and chloric acids at concentrations of the order of those prevailing after insolation caused no detectable liberation of iodine from the potassium iodide. Owing to the volatility of chlorine, concordant results could only be obtained if great care were exercised during pipetting and transference. In the later work, the pipette designed by Jakowkin (*loc. cit.*) was used with advantage.

Chloric acid was determined by the Bunsen method, using

* The paper of Richardson, in which the formation of ozonised oxygen is recorded, was not read until this work was finished, and the point has not yet been tested.

$N/10$-ferrous sulphate and $N/10$-potassium permanganate solutions.
A certain amount of trouble was experienced at the start in dealing
with *partly* decomposed solutions containing both free chlorine
and chloric acid. Attempts to determine chlorine plus chlorate
by the ferrous sulphate method failed. Titration of chlorate by
titanous chloride gave an unsatisfactory end-point, the percentage
error involved being too great in the case of the dilute solutions used.
We then investigated the addition of substances which would
destroy the hypochlorous acid or chlorine present, without either
attacking the chlorate or leaving behind in the solution something
which would subsequently vitiate the chlorate determination (as
was the case when the chlorine was titrated with potassium iodide
and sodium thiosulphate or with sodium arsenite). Manganous
sulphate, urea, and oxalic acid were all found to be possible reagents.
Oxalic acid was chosen, as it seemed feasible that, by its use, both
$Cl_2(HClO)$ and $HClO_3$ might be determined on a single sample.
The general procedure was to pipette 10 c.c. of the solution into a
conical flask, to add 20—40 c.c. of $N/10$-oxalic acid, and to warm
slowly until nearly boiling, adding about 20—30 c.c. of dilute
sulphuric acid towards the end of the heating, which should take at
least 10 minutes. The excess of oxalic acid was then titrated with
$N/10$-permanganate to a faint pink colour, and the chloric acid
determined in the usual way. Appropriate experiments showed
(a) that no formation of chloric acid took place during the reduction
of the $Cl_2(HClO)$, and (b) that, with the concentrations used, the
above procedure resulted in no loss of chloric acid by interaction
with the oxalic acid, as is the case with stronger solutions (Bray,
Z. physikal. Chem., 1906, **54**, 463, 569, 731). Losses of the order of
5—10% of the total soon, however, appeared if the solutions were too
concentrated or too rapidly heated during the oxalic acid treatment,
and, until this was appreciated, concordant results were not obtained.

Further experiments showed that the presence of mercuric
chloride and of the other salts added during the work did not affect
the accuracy of the chlorate determination, with the exception of
$2N$-sodium acetate, when the results were about 1% too low. It
was mentioned above that it seemed possible to determine both
chlorate and $HClO(Cl_2)$ *on the same sample* by this method, the
condition being of course quantitative oxidation of the oxalic acid
according to the equations

$$H_2C_2O_4 + HClO \longrightarrow HCl + 2CO_2 + H_2O$$
$$H_2C_2O_4 + Cl_2 \longrightarrow 2HCl + 2CO_2.$$
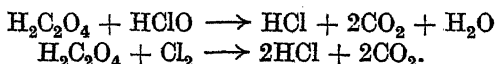
Using an *uninsolated* solution of hypochlorous acid, this was
found to be the case, very concordant results being obtained from

analyses by the oxalic acid, iodide and thiosulphate, and sodium arsenite methods.   With *insolated* solutions of hypochlorous acid or with chlorine water, however, the results were found to average about 4% too low, due in all probability to volatilisation of chlorine before complete reaction.   In the great majority of the experiments, including all those carried out with chlorine water, separate samples were used for the $Cl_2(HClO)$ and $HClO_3$ determinations.

·   *Dark Experiments.*—The following solutions, of oxidising power varying between $0.05N$ and $0.12N$, were sealed up in glass tubes, kept in the dark for periods varying between 2 and 20 days, and subsequently titrated : Hypochlorous acid dissolved in water, in $M/4$-disodium hydrogen phosphate and in $N/2$-sodium acetate; chlorine dissolved in water and in 5% mercuric chloride, 10% nickel sulphate, 10% cobalt sulphate, and 5% lithium sulphate. As always, the greatest care had to be exercised in the manipulation and transference of the solutions containing chlorine, if significant results were to be obtained, these being very readily masked by volatilisation losses caused during pouring, pipetting, etc.   The results showed losses in $Cl_2(HClO)$ titre varying between $0.002N$— $0.009N$ per 24 hours, except in the cases of the chlorine–cobalt sulphate and hypochlorous acid–sodium acetate mixtures.   Such small figures show that the dark reaction can be neglected when carrying out the light experiments.   In the case of the two exceptions, the titre fell per day by amounts varying between $0.02N$— $0.075N$.   A black precipitate was formed in the cobalt sulphate solution.   The results in the case of the hypochlorous acid–sodium acetate mixture will be quoted later.

·   *Apparatus.*—All the definitive experiments were carried out with 110-volt Cooper-Hewitt quartz mercury lamps of the straight tube pattern.   Two kinds of insolation cell were used.   The first and simpler type consisted of a clear silica flask of about 130 c.c. capacity, closed by a rubber stopper.   In the first experiments, the light from the lamp passed successively through a 1 cm. quartz water-cell and an aperture in a hollow copper screen, a stream of water at constant temperature being taken through the screen and a copper condenser on the neck of the flask, finally running out over the surface of the flask to waste.   It was found later that a stream of tap-water playing over the surface of the flask sufficed to keep the temperature constant.   The rubber stopper carried two capillary tubes.   One of these in the earlier experiments led down to the bottom of the flask, and was used for saturating the photolyte with oxygen before-hand, a process which was soon discontinued.   It was closed by pressure tubing and a screw-clip during insolation.   The second was fused on to a three-way tap at the top of a small, water-jacketed

gas burette, provided with a levelling tube and filled with potassium iodide solution. To avoid the manipulation errors already referred to, the chlorine solutions used were finally prepared in the flask, a sample being withdrawn for analysis before insolation.

In carrying out an experiment, the flask was almost filled with the solution under study, put into connexion with the gas burette, and the latter levelled off and read after temperature equilibrium had been reached. The lamp was then lighted, the insolation proceeded with, and burette readings taken at intervals. When the volumes of oxygen collected became too large, they were discharged into the air by the three-way tap, and readings re-started without interrupting the insolation. Sometimes this was carried to completion— sometimes interrupted for a few moments in order to pipette out a sample for analysis, in which case it was necessary to disconnect the burette from the flask. At the end of the experiment, any iodine liberated from the potassium iodide in the burette by chlorine carried over with the oxygen was titrated, and a correction applied.

A large number of experiments were done with this apparatus. The use of a rubber stopper is open to objection. The necessity of disconnecting flask and burette for the purpose of withdrawing a sample for analysis was a disadvantage. So also was the comparatively large dead-space left in the apparatus after removing a sample for titration before insolation, as the chlorine contained in the vapour phase thus produced only slowly diffused along into the potassium iodide solution in the gas burette, rendering the correction correspondingly uncertain. The results were less concordant amongst themselves than those obtained with the cell now to be described, although agreeing sufficiently with the latter.

The cell used in the later experiments consisted of a rectangular glass block $10 \times 10 \times 5$ cm., through which had been drilled a horizontal cylindrical hole, $7 \cdot 5$ cm. in diameter. This hole was closed back and front by circular windows of crystal quartz, cemented to the plane surface of the glass block by a hard pitch composition, special experiments showing that no appreciable reaction took place between dissolved chlorine and the very small surface of cement exposed to its action. In the top of the cell, two openings were drilled. One, closed by a ground-glass stopper, served for the introduction of a pipette for taking samples, etc. The other was closed by a water-sealed, ground-glass joint, bearing a capillary tube connexion sealed on to the gas burette. A similar cell, 2 cm. in depth, served as a water-filter to cut out heat rays. In some experiments, it was directly attached to the front quartz plate of the reaction vessel, thus forming a compound cell, and economising a quartz plate. Experiments showed that, in this

case, there was never more than 0·5° difference between the temperature of the water flowing through the filter and that of the liquid in the reaction cell.

As the work proceeded, continual minor improvements in technique were made. The most concordant results were obtained when the dead-space in the insolation cell was reduced to a minimum (about 3 c.c.).* The solution under investigation was prepared in a stock bottle, and siphoned off into the cell. The latter was first of all rinsed out several times with about 10 c.c. of the liquid, and a vapour phase thus established. It was then filled and, after pipetting out 20 c.c. for analysis, refilled from the stock bottle. In addition, the gas leaving the cell was caused to pass *through* two small traps containing potassium iodide solution, the gas burette being filled with water. After the completion of the experiment, any chlorine in the connecting tubes was gently blown through the potassium iodide traps, the first of which in practice sufficed for complete absorption.

Supersaturation Effects.—It was at first thought that it might be possible to follow the rate of reaction during insolation by means of the volume of oxygen collected at any instant, but it was soon found that this was out of the question, owing to the remarkable extent to which supersaturation occurred. The rate of evolution of gas was, of course, low at the start, owing to the necessity of first saturating the photolyte. It usually increased to a more or less constant value after 2—3 hours. If insolation were interrupted before complete decomposition, then gas continued to come off at the same rate for another 2—3 hours, and only after many hours' standing did the volume become constant. If insolation were continued until all the $HClO(Cl_2)$ had reacted, the rate of collection of gas became less towards the end, corresponding with the decreased light absorption and rate of decomposition. But the liberation of oxygen after the light was cut off still persisted. Careful experiments showed that there was no change taking place in the electrolyte, the oxidising titre of which remained quite unaltered in the dark. The reaction therefore does not exhibit an " after effect." Saturation with oxygen beforehand made no essential difference, not even to the initial time required for the rate of gas evolution to become approximately constant.

The nature of the surface of the containing vessel, on the other hand, had an effect. Gas could be seen coming off at definite points

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* At the beginning of the work the dead-space was carefully shielded from light, in order to avoid the possibility of the reaction $2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2$ taking place in the vapour phase. Work done in another connexion in the laboratory showed this precaution to be unnecessary.

on the surface, and the delayed evolution was more marked with experiments carried out in the smooth silica flasks than was the case when using the composite cells with their inner surface of ground-glass. When sand or powdered quartzite was added to the insolation cell, the rate of gas evolution was still further increased, but its appearance in quantity subsequent to the insolation was never eliminated.

The consequence of the phenomenon was that the sum of the amount of oxygen collected as gas and of that contained in the chloric acid found after the experiment was very seldom (within the experimental error) equal to that calculated from the loss in titre of $Cl_2(HClO)$, even when the solution was left standing for hours after the experiment. The deficiency could easily amount to 30% of the whole. As the formation of perchloric acid had been reported by Billitzer, we tested for this substance in the insolated solution after neutralisation with alkali, using the reaction with methylene-blue described by Monnier (*Ann. Chim. Analyt.*, 1916, **20**, 237). None was ever found, nor, it may be mentioned here, did the usual tests ever show the presence of hydrogen peroxide,[*] the formation of which had been mentioned by Gore. In order to get more positive evidence, experiments were done in which the solution was either allowed to stand for very considerable periods after the insolation, or in which the apparatus was vigorously shaken before the final reading was taken. The following are specimens of the results obtained.

Initial titre.	Final corrected titre.	Corrected loss in titre.	Titre of chloric acid formed.	Titre of oxygen.	Chloric acid plus oxygen.
$0.095N$-HClO	$0.0025N$	$0.0925N$	$0.059N$	$0.032N$	$0.091N$
$0.0935N$-Cl_2	$0.0047N$	$0.0888N$	$0.0563N$	$0.0313N$	$0.0876N$

It was further shown, on several occasions, that, after complete decomposition of a solution of hypochlorous acid, all the chlorine originally present as hypochlorous acid (allowing for losses by volatilisation) was to be found in the solution either as chloric acid or as hydrochloric acid, thus showing that any formation of perchloric acid was negligible. It seems therefore reasonable to suppose that supersaturation is solely responsible for the observed phenomena, and that there is neither an "induction period" nor an "after-effect," as Draper had imagined.

Certain remarkable experiments should, however, be especially mentioned, in which chlorine water and chlorine water containing

[*] Observations of Anderson and Taylor (*J. Amer. Chem. Soc.*, 1923, **45**, 1215) render it unlikely that appreciable amounts of hydrogen peroxide could exist under our experimental conditions.

dissolved mercuric chloride were insolated in a silica flask. Practically no gas could be seen coming off from the solutions during irradiation and, in the whole set of about twenty-five experiments, more than 2 c.c. of oxygen were never collected during any single insolation, although amounts of up to 50 c.c. would have been anticipated from the subsequent analyses for chloric acid and negative tests for perchloric acid. After completion of the experiments, the solutions were in some cases boiled or evacuated, but not more than an extra c.c. of gas was ever obtained. This curious non-appearance of gas remains unexplained. It is, of course, possible to imagine the gas being given off from the liquid surface as single molecules or small aggregates, instead of being liberated as visible bubbles. It is also true that the neck of the flask was closed by a rubber stopper, which might conceivably react with any " activated " oxygen or ozone, but the suggestion would seem inadequate to explain such a complete elimination of the appearance of oxygen. It may be added that of course the possibilities of a leak or of the presence of some reducing agent in the apparatus were carefully gone into. In any case, the striking feature of the experiments to the eye was the absence of visible oxygen evolution. It is hoped to follow up the subject further. In the meantime, it may be mentioned that relevant data are contained in the recent papers by Metschl (*J. Physical Chem.*, 1924, **28**, 427) and by Kenrick, Wismer, and Wyatt (*ibid.*, p. 1314).

Results.

The figures which follow represent the percentages of chlorine or hypochlorous acid which, on reaction, gave chloric acid as a product. The remainder, in absence of any positive test for perchloric acid or hydrogen peroxide, is assumed to have decomposed, giving oxygen.

Chlorine Water.—Several series of measurements, during which the experimental technique was gradually improved, were carried out, involving nearly fifty different insolations.

Series.	Type of apparatus.	No. of expts.	Extreme values.	Mean value.
1	Flask	9	56·3—68·3	62·5
2	Cell	6	57·4—62·3	60·1
3	Flask	3	58 —66	63
4	Flask	13	51 —76	60·4
5	Cell	3	55 —63	60
6	Cell	12	59 —63	61·3

The general mean is 61·2% of chloric acid, which is also practically the mean of the last and most concordant series. The strengths of the solutions insolated varied between $0·158N$ and $0·0175N$, and

the degree of decomposition from about 15% to completion. The extreme values for the chloric acid figures were obtained either when the technique had not been fully developed, or when the titration values were very small, and the errors correspondingly great. We therefore feel justified in concluding that the proportions of the products are not sensibly affected either by the initial concentration or by the extent of decomposition.

Chlorine in Hydrochloric Acid Solution.*—

Conc. of HCl	0·004N	0·01N	0·1N	0·5N
Chloric acid % ...	56	55·5	31·7; *29*; 27	22·5; 10; *14*

Chlorine in Potassium Chloride Solution.*—

Conc. of KCl	0·1N	0·5N
Chloric acid %	51·9; *60*; 63; 45	44·3; *29*; 21; 15; 26

Chlorine in Mercuric Chloride Solution.—As with chlorine water, several series of measurements were done, the concentration of the mercuric chloride always being 5%. As aqueous mercuric chloride is reported by some observers to be photosensitive, with formation of calomel and evolution of oxygen (*e.g.*, Pougnet, *Compt. rend.*, 1915, **161**, 348), solutions containing the salt alone were insolated beforehand, but no trace of decomposition could be detected. This agrees with the observation of Lesure (*J. Pharm. Chim.*, 1910, **1**, 569).

Series.	Type of apparatus.	No. of expts.	Extreme values.	Mean value.
1	Flask	3	55—68	60·3
2	Flask	13	57—79	65
3	Cell	4	65—66	65·2
4	Cell	3	62—63·5	62·8

The general mean gives 64·1% of chloric acid.

Chlorine in other Chloride Solutions.—

Solution	0·01M-CdCl$_2$	0·1M-CdCl$_2$	0·5M-CdCl$_2$	0·5N-LiCl
Chloric acid %......	55·7	57·9	44·6	39

Chlorine in Sulphuric Acid Solution.—

Conc. of H$_2$SO$_4$.	Chloric acid %.
0·1N	57·6; 64·2; 49·5; 62; 63; 57; 63 (mean figure 59·5)
0·5N	52·6; 48; 57; 59; 60; 61 (mean figure 56·3)

There appeared to be a certain tendency in this case for solutions containing higher initial chlorine concentrations to give lower chloric acid percentages.

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* Many of the titration figures for chlorate were here exceedingly small —the percentages given in italics correspond to the largest, and hence presumably to the most trustworthy, titrations.

Chlorine in Sodium Sulphate Solution.—

Conc. of Na$_2$SO$_4$ ...	0·01M	0·1M	0·33M	Saturated
Chloric acid %	63·2	60·0	62·5; 62; 62	61·7

Mean figure 61·9

Chlorine in Lithium Sulphate Solution.—

Conc. of Li$_2$SO$_4$	0·25M	0·5M	1M	2M
Chloric acid %	63	67	69	73; 73

The colour of solutions of chlorine in aqueous sodium and lithium sulphates is far less pronounced than is the case with chlorine water alone, or with chlorine dissolved in dilute solutions of sulphuric acid or of halides.

Chlorine in other Solutions.—

Added solute	Bromine	0·5%CuSO$_4$	0·5%CoSO$_4$	0·5%NiSO$_4$
Chloric acid %	61·3	64; 63; 64	61·5; 56	59; 67

An experiment with chlorine dissolved in 0·5% manganous sulphate resulted in the rapid formation of a black precipitate, the same slowly occurring in the dark. In certain circumstances, the solution in cobalt sulphate behaved similarly.

*Hypochlorous Acid.—*Five experiments gave 65·3; 63·4; 57; 58; 60·2% of chloric acid (mean figure 60·8).

*Hypochlorous Acid in Sodium Phosphate Solution.—*Two experiments gave 81% in 0·25M- and 86% in 0·125M-disodium hydrogen phosphate.

*Hypochlorous Acid in Sodium Acetate Solution.—*It was mentioned earlier that experiment showed the dark reaction in this case to be considerable, a 0·1N-hypochlorous acid solution in 0·5N-sodium acetate losing about half its titre in 9 days. It soon became apparent that the light reaction itself was more complex than those hitherto studied. Two insolations were made of solutions of about the same composition as above. They rapidly lost their titre when exposed to light, but no evolution of oxygen could be detected in the one case, and the merest trace in the other, whilst subsequent analyses showed only 12 and 18%, respectively, of the original oxidising power as chloric acid. Chlorination or oxidation of the sodium acetate or of the acetic acid formed in the reaction naturally suggested itself, and the usual tests were applied for monochloroacetic, succinic, and oxalic acids. All were negative, although an appropriate amount of the substance concerned gave a positive result under the conditions of experiment. However, on boiling with alcoholic potash, after adding a drop of aniline, a faint but unmistakable smell of carbylamine was noticed, which pointed to the presence of chloroform. This observation probably means that hypochlorous acid chlorinates acetic acid or sodium acetate in light

to give trichloroacetic acid, the chloroform either being formed during the carbylamine test, or possibly being produced by the further action of light on the trichloroacetic acid *in statu nascendi*. The formation of the monochloro- and dichloro-acids is presumably transitory, as no trace of oxalic acid, which would be the final product of their photolysis under the experimental conditions, was found.

In order roughly to check the results, another insolation was carried out in which, after partial decomposition of the hypochlorous acid and determination of the chloric acid (which amounted to 24% of the loss in HClO titre), the chloride concentration of the solution which had been used in the chlorate analysis was determined by titration. The result, of course, represented the total chlorine present in the original solution, less that fixed (presumably) as trichloroacetic acid. The figures were (expressed as gram-atoms or gram-ions per litre)

Cl in original HClO	....	0·0622
Cl as HClO after insolation	...	0·0250
Cl converted to $HClO_3$	......	0·0029
Cl' found on titration	....	0·0397
Hence Cl as Cl' after insolation	......	$0·0397 - 0·0250 - 0·0029 = 0·0118$
Cl fixed as $CCl_3 \cdot CO_2H$ (?)	...	$0·0622 - 0·0397 = 0·0225$

Another portion of the insolated solution was then taken, hydrolysed by 12·5% sodium hydroxide, and another chloride titration carried out. This figure (corrected for a blank test on the sodium hydroxide) should be a measure of the chloride formed during the insolation and by the hydrolysis, plus that produced on heating the alkaline sodium hypochlorite, in accordance with the reaction

$$3ClO' \longrightarrow 2Cl' + ClO_3'.$$

The result was 0·0542N. If we add the figures for the chlorine converted to chlorate ion during the insolation (0·0029N) and during the hydrolysis (0·0083N, if the above equation is correct), we get a total of 0·0654N, compared with the figure of 0·0622N in the 0·1244N-hypochlorous acid taken. The discrepancy of 5% is reasonable considering the assumptions made. Thus, for example, it is conceivable that, during the hydrolysis, further chlorination of the acetate by hypochlorite ions may have occurred, or possibly decomposition in accordance with the equation

$$2ClO' \longrightarrow 2Cl' + O_2,$$
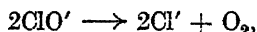
either of which reactions would have caused a discrepancy in the sense found.

One further experiment was done, in which a dilute—0·5%—solution of sodium acetate was used, and the mixture with 0·045N-hypochlorous acid exposed to daylight for 10½ hours. The chloric

acid percentage of the loss in hypochlorous acid titre was now found to be 72, a very different figure from those given by strong sodium acetate solutions. Chloride determinations were carried out as above, and good agreement was found with the calculated figure. It would thus appear definitely as if, on insolating these solutions, two reactions proceed simultaneously—photodecomposition of the hypochlorous acid, resulting in the production of much chloric acid and little oxygen, and chlorination of the added acetate, the latter reaction naturally occurring to a greater extent the higher the percentage of acetate present. Time has not yet permitted of a further investigation of these results.

Effect of Wave-length.—Experiments carried out in sunlight, diffused daylight, and in monochromatic light of wave-lengths 313, 365, and 436 $\mu\mu$ showed no appreciable difference in the proportion of the products formed.

Effect of Surface.—Two experiments on solutions of hypochlorous acid indicated that, in presence of the highly developed surface furnished by adding pure silica powder to the contents of the insolation vessel, the proportion of chloric acid in the product was considerably reduced. In the present lack of confirmatory experiments, we prefer to lay no stress on this observation.

Discussion.

A detailed discussion of the mechanism of the reaction is best postponed until the measurements on the energetics have been described. Certain conclusions can, however, be drawn at this stage. The results obtained with the solutions of hypochlorous acid in disodium hydrogen phosphate, *viz.*, an increase in the chloric acid yield from 61 to 83%, support our assumption that oxygen atoms are the primary product of photolysis, and that molecules of hypochlorous acid present will act as acceptors for these oxygen atoms, or possibly for "activated" oxygen molecules, the final result being formation of chloric acid. That the addition of disodium hydrogen phosphate to the hypochlorous acid solutions did, in fact, prevent the formation of hydrochloric acid and thus of free chlorine during the insolation is made very probable by the fact that such solutions remained colourless throughout the experiment. Further, when chlorine was passed into a solution of disodium hydrogen phosphate, the initial yellow colour disappeared on standing for a short time, and on addition of potassium iodide, the solution behaved like hypochlorous acid, *i.e.*, it required added mineral acid in order to liberate its full amount of iodine. The uncertainty as to whether there was appreciable formation of hypochlorite *ions* has already been mentioned. One fact, however, speaks against this, as Mr.

M. Holmes, working in this laboratory on the photodecomposition of sodium hypochlorite solutions, found only 11—12% chlorate formation, indicating that hypochlorite ions are not very avid acceptors of oxygen atoms (or " activated " oxygen molecules). The results with sodium acetate solutions are perhaps less conclusive, in consequence of the simultaneous photochlorination which is going on. Nevertheless, the amount of oxygen set free in this case is negligible compared with the quantity of chloric acid produced. It is also noticeable that solutions of chlorine in aqueous lithium sulphate, which became more nearly colourless as the concentration of the salt was increased, gave corresponding progressively increasing yields of chloric acid.

When we consider the results obtained with chlorine water, however, particularly those given by solutions of chlorine in dilute hydrochloric acid, the facts by no means completely fit the original hypothesis. This was, briefly, that the only products, or practically so, of the photo-reaction between chlorine itself and water are *oxygen* and hydrochloric acid, and therefore that, if by addition of hydrochloric acid to the chlorine water beforehand, the amount of hypochlorous acid in the photolyte could be made negligible, there should be only a correspondingly minute quantity of chloric acid present after insolation. This, however, is not so.

The value of the Jakowkin equilibrium constant, $K = [Cl_2]/[H^{\cdot}][Cl'][HClO]$, is about 2500 at 20°, concentrations being expressed as mols./litre (Gröh, *Z. physikal. Chem.*, 1913, **81**, 695; see also Lewis and Randall, " Thermodynamics," p. 508). Assuming complete dissociation of any hydrochloric acid added or formed by hydrolysis, we have calculated the approximate concentrations (before insolation) of the various constituents present in $0.1N$ $(0.05M)$-chlorine, dissolved in water and in $0.01N$-, $0.1N$-, and $0.5N$-hydrochloric acid. The results are contained in the following table, together with the percentage yield of chlorate experimentally found :—

Solution insolated.	Fraction of chlorine hydrolysed.	[HCl].	[HClO].	[Cl$_2$].	Percentage chloric acid yield.
$0.05M$-Cl$_2$	0·45	0·0225	0·0225	0·0275	61
„ + 0·01N-HCl	0·35	0·0275	0·0175	0·0325	55*
„ + 0·1N-HCl	0·04	0·102	0·002	0·048	29†
„ + 0·5N-HCl	0·0015	0·500	0·000075	0·0499	14†

One insolation only. † " Best " values.

It is clear that the chloric acid yield falls off far less rapidly than is likely to have been the case if it were solely produced by interaction between primarily formed oxygen and hypochlorous acid molecules present at concentrations demanded by the Jakowkin

constant. It would appear possible that hypochlorous acid is one
of the intermediate products of reaction of photo-activated chlorine
molecules with water, this photo-product acting as an acceptor for
the oxygen. A somewhat similar mechanism was proposed by
Billitzer. The effect of an increased concentration of hydrogen
chloride would, of course, then be, by re-formation of chlorine, to
lower the " stationary state " concentration of the hypochlorous
acid, and thereby to decrease the opportunity for formation of
chloric acid.

With regard to the results obtained with the other salts, addition
of either potassium chloride, lithium chloride, or cadmium chloride
lowers the chloric acid yield, but in a lesser degree than does hydro-
chloric acid, a result to be anticipated (qualitatively) from the
Jakowkin equation. Potassium chloride would appear (in $0.5N$-
solution) to have the greatest effect, but the experiments are too
few to enable any definite conclusions to be drawn. There is no
doubt, however, that the action of sulphuric acid is, in this respect,
much less than that of potassium chloride. This in itself is enough
to show that the Jakowkin equation is by no means the only deter-
mining factor. The different ions appear to have specific effects,
a view which is supported by the marked difference between the
mode of decomposition of chlorine dissolved in sodium sulphate and
in lithium sulphate solution.

From the figures with mercuric chloride solutions, we feel justified
in concluding that the percentage of chloric acid is slightly increased.
This result can be construed (qualitatively) in the light of the
Jakowkin equation, as a rough calculation based on the results of
Luther and of Sherrill shows that the chlorine-ion concentration
in a completely photolysed $0.05M$-chlorine solution is reduced by
about half when the solution contains 5% of added mercuric chloride,
owing to the formation of $HgCl_4''$ ions.

One further striking result should be commented upon. There
is no doubt at all that the presence of small concentrations of
hydrochloric acid (say $0.1N$ or less) added to chlorine-water solutions
before insolation depresses the yield of chloric acid. On the other
hand, no diminution in this yield during the insolation of a chlorine-
water solution was ever observed, in spite of the fact that the
concentration of hydrogen chloride was continually increasing.
Still more remarkable is the fact that the percentage of chloric acid
produced during photolysis of a solution of hypochlorous acid is
identical with that given by chlorine water. Putting, for the sake
of simplicity, the percentage of chloric acid given by $0.1N$-solutions
of both substances as 60 (actually 61), the stoicheiometric equations
for the two photodecompositions are :

$$0.05Cl_2 + 0.05H_2O \longrightarrow 0.01HClO_3 + 0.09HCl + 0.01O_2$$
$$0.05HClO \longrightarrow 0.01HClO_3 + 0.04HCl + 0.01O_2$$
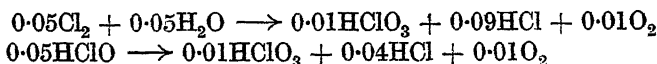
equations which apparently hold whatever the degree of decomposition, and the former of which corresponds to that given by Popper for the decomposition of chlorine water. Thus a reduction of the final hydrochloric acid acidity by more than half makes no difference in the yield of chloric acid, while, on the other hand, if the final acidity is doubled by working with chlorine solutions with $0.1N$-hydrochloric acid added, or suppressed by adding disodium hydrogen phosphate to hypochlorous acid solution, the chlorate percentage falls to about 30 or rises to more than 80, respectively.

Using the same value of the Jakowkin equilibrium constant and the same assumptions as previously, we have calculated the values of [HCl] in a number of solutions before insolation, half way through the insolation, and after complete decomposition. The results are contained in the following table.

Solution insolated.	[HCl] at start.	[HCl] after 50% decomp.	[HCl] at end.	Yield of chloric acid %.
$0.05M$-HClO + Na$_2$HPO$_4$	—	—	—	83
$0.05M$-HClO	—	0.013	0.04	61
$0.05M$-Cl$_2$	0.0225	0.0487	0.09	61
,, + 0.01N-HCl	0.0275	0.0575	0.10	55
,, + 0.1N-HCl	0.102	0.1455	0.19	29
,, + 0.5N-HCl	0.500	0.545	0.59	14

It is difficult at first sight to see why the solutions of $0.05M$-hypochlorous acid and $0.05M$-chlorine should give the same yield of chloric acid when the HCl acidity conditions are so different. We are inclined to attribute it to the fact that, as soon as decomposition of the hypochlorous acid has commenced, chlorine will be formed in the first layers of the cell. The solutions were not stirred during the experiments, owing to the volatility of the substances present. Consequently the first and absorbing layers will be different in composition from the solution in the rest of the cell, which is unaffected or only weakly affected by light. They will always contain more acid than the latter, and a high chlorine concentration in comparison with their hypochlorous acid content. Chlorine, moreover, absorbs far more strongly than hypochlorous acid. So that the solution is really being insolated under conditions which, both in respect of acidity and of nature of absorbing molecules, correspond far more closely to those in a chlorine-water solution than at first sight they appear to do. This seems a very possible explanation of the results observed.

With regard to the first stage of the reaction in these experiments, we have no doubt that both the hypochlorous acid and the chlorine

molecules are primarily photosensitive. All the experiments go to show this, and we cannot agree with the view expressed by Benrath and Schaffganz that the hypochlorite ion is the sole responsible photosensitive agent. Its concentration in $0.05M$-hypochlorous acid is of the order of 2×10^{-5} and in $0.05M$-chlorine about 10^{-8} equivalents/litre. Further experiments in this laboratory have shown that the quantum efficiency for the decomposition of a $0.06N$-solution of sodium hypochlorite is about the same as for hypochlorous acid and for chlorine water, and we regard it as in the highest degree unlikely that this agreement would be obtained if, in all these solutions, the hypochlorite ion, with its widely different concentrations, were the sole photosensitive component.

Summary.

(1) The apparatus and experimental methods used in the investigation of the photodecomposition of chlorine water and hypochlorous acid solutions are described.

(2) It is shown that, except when substances are added which cause secondary reactions, the sole products of decomposition are hydrochloric and chloric acids and oxygen.

(3) Results are tabulated showing the percentage yield of chloric acid obtained in photolysis of chlorine water; chlorine water containing certain added acids, salts, etc.; hypochlorous acid; and hypochlorous acid containing added . disodium hydrogen phosphate or sodium acetate.

(4) Secondary reactions were found with chlorine water containing manganese sulphate or cobalt sulphate (sometimes), and with mixtures of hypochlorous acid and sodium acetate.

(5) The results show that both the hypochlorous acid and the chlorine molecule are photosensitive, the latter possibly giving hypochlorous acid as a primary product. The evidence indicates that some at all events of the ions present in the salts used have a specific effect on the proportions of the products.

CXVIII.—*The Composition of the Liquid and Vapour Phases of Mixtures of Glycerol and Water.*

By MANATHATTAI PICHU IYER VENKATARAMA IYER and
FRANCIS LAWRY USHER.

SINCE information about the loss of glycerol on evaporation of its concentrated solutions could not be found in the literature, we made the necessary measurements, and the results are now recorded.

Material.—The " chemically pure glycerine " (Merck) used contained no appreciable quantity of foreign substances, except water. A sample was distilled, and the first and the last fraction were free from volatile organic impurities and polyglycerols, respectively.

Method.—The proportion of glycerol in the vapour phase of mixtures of water and glycerol containing less than 75% of the latter is negligible. Solutions of high glycerol content rapidly change in composition when partly vaporised, and therefore the method of examination must involve not only the formation of as little vapour as possible, but also the rigorous prevention of any fractional condensation of it when once formed. A simple arrangement was used in which the possibility of such condensation was eliminated. The compositions of the liquid and of the condensed vapour were determined refractometrically.
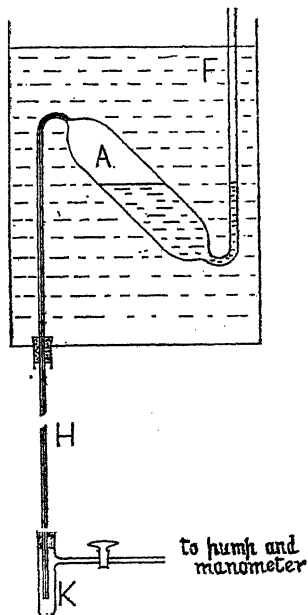
A wide glass tube, A (see fig.), of about 300 c.c. capacity, which was used as the still, was sealed at its upper end to a length of thermometer tubing, H, and at its lower end to a tube, F, of about 5 mm. bore, through which the liquid was admitted or withdrawn. The still, set at an angle of 45°, was completely immersed in a large brine bath, the tubes F and H pointing vertically upwards and downwards, respectively. The latter, held by a cork in a tubulure in the floor of the bath, extended for about 50 cm. below the bath and passed through a rubber stopper fitting into a small receiver, K, which communicated, through a tapped side tube, with a Fleuss pump and a manometer.

About 180 c.c. of a glycerol-water mixture having been intro-

duced into A through the tube F, this was closed by stout rubber tubing carrying a screw-clamp, the apparatus was thoroughly exhausted through the side tube of K, and the tap closed. Burners placed outside the bath were regulated so that there was an upward temperature gradient from the bottom to the top (any condensation in the still thus being prevented). When a convenient quantity of liquid had collected in K—which always remained cold—the experiment was stopped by admitting air through F, and the condensate was immediately examined.

At the commencement and at the end of each experiment, a sample of the liquid in A was withdrawn by a pipette and analysed; the mean was taken as the composition of the mixture corresponding with the vapour condensed.

The liquid in A was stirred by admitting bubbles of air through F. The efficacy of the method was proved by introducing, one above the other, two mixtures of widely different composition into the still, and withdrawing successive samples while a slow stream of air was being drawn through the liquid; constancy of composition was rapidly attained. Owing to the slope of the still, no liquid was carried over into the capillary tube, and no error from this source is to be feared : indeed, the presence of a very small quantity of the main liquid in the condensate would be at once evident from the composition of the latter; but in nearly every case the points representing the composition of the vapour fell, within the limits of experimental error, on a regular curve.

Three methods suggest themselves for the determination of the composition of mixtures containing only glycerol and water : the measurement of the density, the estimation of the glycerol by chemical means, and the measurement of the refractive index. The first two were rejected as requiring an inconveniently large quantity of material, and the third was adopted. Since the temperature of the tap-water used for jacketing the prisms of the refractometer was 23—24°, the measurements were, for convenience, carried out at 25°. No trustworthy data for the refractive index of glycerol solutions at 25° are available, and the necessary measurements were therefore carried out. The density of the original sample of glycerol at 20° showed it to contain 97·75% of glycerol, and this liquid was used for the preparation of a series of solutions having a lower glycerol content, the dilution being carried out in dry stoppered bottles with known weights of water and the original solution. From time to time the compositions of these solutions were checked by density measurements. The solutions were examined in an Abbé (Hilger) refractometer at 25°, and a composition–refractive index curve was drawn. The transference of

samples of solutions of high glycerol content to the refractometer prism by means of a fine-pointed pipette did not occupy more than 2 or 3 seconds and no appreciable absorption of moisture could have occurred. The liquid, when once secured between the prisms, showed a constant refractive index for at least 10 minutes after it had attained the temperature of the water-jacket, whereas the time required to make the series of settings and readings (usually six) was less than 2 minutes. The sample of 100% glycerol was obtained by bubbling a stream of dry air through the 97·75% solution maintained at about 90°, until the refractive index attained a constant value.

Accuracy of the Results.—The accuracy of the results is affected mainly by one source of error, which is to some extent unavoidable in working with solutions of high glycerol content. Such solutions, yielding a vapour which consists largely of water, necessarily undergo on distillation a change in composition which is great compared with that attending the partial vaporisation of mixtures whose constituents have boiling points differing by a much smaller interval of temperature. This change in composition increases as the proportion of glycerol rises, and all that can be done to mitigate its effect on the accuracy of the results is (1) to vaporise as little of the liquid as possible, consistently with securing a fair sample, and (2) to take the mean of the compositions of the liquid before and after vaporisation. In any experiment in which a vapour phase is present, fractional condensation must occur in the receiver, but the error thus introduced may be neglected if the mass of vapour condensed is large compared with that remaining uncondensed. In our experiments this condition was secured by using a very small receiving system, the total volume of which was less than 20 c.c., whereas the amount of condensate varied from about 0·1 to 0·25 g., so that all but a fraction of 1% of the vapour was actually condensed, and the liquid so obtained could reasonably be considered a fair sample. Thirty-eight determinations were made, and a smooth curve was drawn through the points obtained by plotting the composition of the vapour against that of the liquid. A rapid change occurs in the composition of the vapour from solutions containing about 98% of glycerol, and therefore the curve had to be drawn through the experimental values for 98 and 99% glycerol. The value given for 99% glycerol may be as much as 2 or 3% in error, since the curve is very steep here, and no measurements could be made at higher concentrations; otherwise the maximum deviation of the experimental figures from those given by the curve is equivalent to 0·15% of glycerol. The following tables show (1) the corresponding percentages of glycerol by

weight in liquid and vapour for mixtures containing 75% of glycerol and more; and (2) the refractive indices of mixtures of glycerol and water at 25°.

Percentage of glycerol in

Liquid phase	75	80	85	86	87	88	89
Vapour phase	0·2	0·3	0·4	0·45	0·45	0·5	0·55
Liquid phase	90	91	92	93	94	95	96
Vapour phase	0·55	0·6	0·65	0·7	0·75	0·85	0·95
Liquid phase	97	98	99	100			
Vapour phase	1·2	1·7	17	100			

Refractive Indices.

Glycerol %	0	5	10	15	20	25	30
$n_D^{25°}$	1·3333	1·3394	1·3455	1·3516	1·3577	1·3641	1·3709
Glycerol %	35	40	45	50	55	60	65
$n_D^{25°}$	1·3777	1·3846	1·3917	1·3985	1·4058	1·4131	1·4204
Glycerol %	70	75	80	85	90	95	100
$n_D^{25°}$	1·4281	1·4357	1·4435	1·4506	1·4576	1·4651	1·4730

CXIX.—*The Isomerism of the Oximes. Part XXI. Action of Picryl Chloride and of* 2 : 4-*Dinitrochlorobenzene on Aldoximes.*

By OSCAR L. BRADY and LOUIS KLEIN.

THE action of 2 : 4-dinitrochlorobenzene on a number of aldoximes was studied by one of us and Truszkowski (J., 1924, 125, 1087); this work has now been extended to the action of picryl chloride, whilst an attempt has been made to elucidate some of the outstanding problems presented by the earlier work.

Dinitrochlorobenzene reacted with the sodium salts of *anti*-aldoximes in a somewhat similar manner to the alkyl halides, giving dinitrophenyl ethers, though these appeared to have the *syn*-configuration; these ethers, like the alkyl ethers, were difficult to hydrolyse with acid, but, whereas the alkyl ethers are stable to alkalis, the dinitrophenyl derivatives were readily decomposed giving the nitrile, thereby resembling the acyl derivatives of the *syn*-aldoximes. With the sodium salts of the *syn*-aldoximes, decomposition occurred with the formation of the aldehyde corresponding to the oxime but no nitrile. As was expected, picryl chloride behaved more like an acyl halide; with the sodium salts of *anti*-aldoximes it gave trinitrophenyl derivatives analogous to acyl derivatives, *e.g.*, the diphenylcarbamyl compounds (compare Brady and Dunn, J., 1913, 103, 1613). These were fairly readily hydrolysed by concentrated hydrochloric acid to picric acid and

the carboxylic acid through the nitrile, or by alkalis to picric acid and the nitrile; if the customary convention is adopted, they must consequently be given the *syn*-configuration :

$$\begin{array}{c} \text{R·CH} \\ \underset{\text{N·O·C}_6\text{H}_2(\text{NO}_2)_3}{\|} \end{array} \longrightarrow (\text{NO}_2)_3\text{C}_6\text{H}_2\text{·OH} + \text{R·CN} \longrightarrow \text{R·CO}_2\text{H}.$$
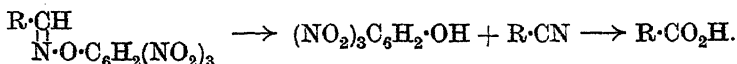
The following picryl derivatives have been prepared from the sodium salts of the corresponding *anti*-aldoximes : picrylbenz*syn*-aldoxime, picryl-*o*-, *m*-, and *p*-nitro-, *o*- and *p*-methoxy-, 3 : 4-methylenedioxy-, *p*-dimethylaminobenz*syn*aldoximes, picrylcinnam-*syn*aldoxime, and picryl-4-picryloxy-3-methoxybenz*syn*aldoxime; no derivative could be obtained from the sodium salts of *o*- and *p*-hydroxybenz*anti*aldoximes.

With the sodium salts of *syn*-aldoximes a mixture of aldehyde and nitrile was obtained. The picryl chloride in this respect is intermediate in its action between dinitrochlorobenzene, which gives the aldehyde, and acetyl chloride, which gives the nitrile, but differs totally from the alkyl halides, which give stable *N*-alkyl compounds, from diphenylcarbamyl chloride, which gives diphenyl-carbamyl derivatives of the *syn*-aldoximes (Brady and Dunn, *loc. cit.*), and from benzoyl chloride, which gives benzoyl derivatives of the *anti*-oximes (Brady and Thomas, J., 1922, **121**, 2104; Brady and Grayson, J., 1924, **125**, 1419; Brady and McHugh, unpublished work).

The mechanism of the reaction of 2 : 4-dinitrochlorobenzene on the sodium salts of the *syn*-aldoximes has been further studied (compare Brady and Truszkowski, *loc. cit.*). It seems most probable that an *N*-substituted derivative is first formed which is immediately hydrolysed to the aldehyde and β-dinitrophenyl-hydroxylamine, the latter unstable compound then decomposing (compare Borsche, *Ber.*, 1923, **56**, 1494) :

$$\begin{array}{c} \text{R·CH} \\ \underset{\text{N·ONa}}{\|} \end{array} + (\text{NO}_2)_2\text{C}_6\text{H}_3\text{Cl} \longrightarrow \begin{array}{c} \text{R·CH} \\ \underset{(\text{NO}_2)_2\text{C}_6\text{H}_3\text{·N:O}}{\|} \end{array} \longrightarrow$$
$$\text{R·CHO} + (\text{NO}_2)_2\text{C}_6\text{H}_3\text{·NH·OH}.$$
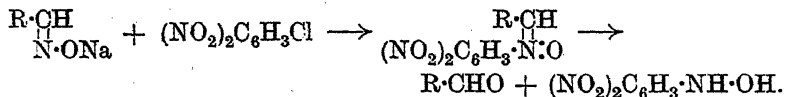
The method of decomposition of the β-dinitrophenylhydroxyl-amine could not be ascertained; the question is discussed in the experimental part (see p. 849).

Brady and Truszkowski (*loc. cit.*) found that 2 : 4-dinitrochloro-benzene gave the same addition compound with both *p*-methoxy-benz*anti*- and *p*-methoxybenz*syn*-aldoxime. Owing to the in-stability of the latter oxime, it seemed possible that isomeric change occurred during the determination of the freezing points, particularly if a trace of hydrogen chloride were produced. The

fusion diagrams of 2 : 4-dinitrochlorobenzene with cinnam*anti*- and cinnam*syn*-aldoximes have been constructed. Although the latter *syn*-aldoxime is much more stable than *p*-methoxybenz*syn*aldoxime and its conversion to the *anti*-isomeride by traces of hydrogen chloride has not been observed, the same addition compound was obtained from both oximes. Moreover, rapid treatment with dilute sodium hydroxide broke up the addition compound into dinitrochlorobenzene and cinnam*anti*aldoxime; this seems to eliminate the possibility that the *anti*- is converted into the *syn*-aldoxime, a view previously entertained, since oximes which were known not to give *syn*-isomerides did not show compound formation with dinitrochlorobenzene.

<div align="center">EXPERIMENTAL.</div>

Action of Picryl Chloride on anti-*Aldoximes.*—Benz*anti*aldoxime (12 g. = 1/10 mol.) was dissolved in warm alcohol (50 c.c.), a solution of sodium (2·3 g. = 1/10 mol.) in alcohol (50 c.c.) added, followed by a solution of picryl chloride (24·7 g. = 1/10 mol.) in warm alcohol (400 c.c.). A red colour developed and the picryl compound soon crystallised; after keeping for an hour, it was separated, and washed first with alcohol then with warm water, when a 70% yield of crude *picrylbenzsynaldoxime* was obtained. Crystallised three times from boiling acetone, it gave canary-yellow prisms, m. p. 181—182° (decomp.) (Found : N = 16·7. $C_{13}H_8O_7N_4$ requires N = 16·9%). Other picryl derivatives were prepared similarly from the corresponding *anti*-aldoximes.

The yields given are those of the crude products after washing and drying. The compounds were crystallised two or three times from boiling acetone unless otherwise stated : *Picryl-*p-*methoxy-benzsynaldoxime* (yield 60%), sulphur-yellow needles, m. p. 142—143° (decomp.) (Found : N = 15·8. $C_{14}H_{10}O_8N_4$ requires N = 15·5%). *Picryl-*o-*methoxybenzsynaldoxime* (yield 100%), pale yellow prisms, m. p. 153—154° (decomp.) (Found : N = 15·9. $C_{14}H_{10}O_8N_4$ requires N = 15·5%). *Picryl-3 : 4-methylenedioxybenzsynaldoxime* (yield 80%), deep yellow, microscopic needles, m. p. 152° (decomp.) (Found : N = 15·0. $C_{14}H_8O_9N_4$ requires N = 14·9%). In the preparation of this compound more alcohol must be used in order to keep the sparingly soluble sodium salt of the oxime in solution. *Picryl-*o-*nitrobenzsynaldoxime* (yield 25%), pale yellow prisms, m. p. 157—158° (decomp.) (Found : N = 18·6. $C_{13}H_7O_9N_5$ requires N = 18·6%). This was more soluble than the other picryl derivatives and was crystallised from dilute acetone. The low yield was due to loss by solution in alcohol. *Picryl-*m-*nitrobenzsynaldoxime* (yield 80%), pale yellow cubes, m. p. 169° (decomp.) (Found : N = 18·7.

$C_{13}H_7O_9N_5$ requires $N = 18.6\%$). *Picryl*-p-*nitrobenzsynaldoxime*
(yield 60%), pale yellow prisms, m. p. 168° (decomp.) (Found :
$N=18.3$. $C_{13}H_7O_9N_5$ requires $N=18.6\%$). *Picryl*-p-*dimethylamino-
benzsynaldoxime* (70% yield), orange-red prisms darkening at 110°
and decomposing at about 130° (Found : $N = 18.5$. $C_{15}H_{13}O_7N_5$
requires $N = 18.7\%$). This compound decomposes in hot acetone
and cannot be crystallised satisfactorily from benzene, alcohol,
chloroform, ether or acetic acid. It was purified by solution in
cold acetone and cooling in ice, followed by the addition of water
drop by drop with scratching until a suitable quantity had crystal-
lised out. *Picrylcinnamsynaldoxime* (yield 65%), pale yellow
prisms, m. p. 164—165° (decomp.) (Found : $N = 16.1$. $C_{15}H_{10}O_7N_4$
requires $N = 15.7\%$). 3-Methoxy-4-hydroxybenz*anti*aldoxime (2.5
g. = 1 equiv.) was dissolved in alcohol (20 c.c.), and a solution of
sodium (0.69 g. = 2 equiv.) in alcohol (20 c.c.) added ; the mixture
was cooled in ice, and treated with a solution of picryl chloride
(7.4 g. = 2 equiv.) in alcohol (100 c.c.), the whole being then
immediately cooled in ice. After some time, the precipitate was
collected and washed as before (yield 34%). Using only one
equivalent each of sodium and of picryl chloride, a much smaller
yield of the same compound was obtained. From acetone solution
on addition of water, *picryl*-3-*methoxy*-4-*picryloxybenzsynaldoxime*
separated in very pale yellow prisms, m. p. 178—179° (decomp.)
(Found : $N = 16.8$. $C_{20}H_{11}O_{15}N_7$ requires $N = 16.6\%$). When a
solution of the sodium salt of *o*- or *p*-hydroxybenz*anti*aldoxime
was treated with picryl chloride, the only reaction which occurred
was the decomposition of the picryl chloride, picric acid and the
oxime being the only compounds recoverable even when 2 mols.
of picryl chloride were employed (compare Brady and Truszkowski,
loc. cit.).

Alkaline Hydrolysis of Picrylbenzsynaldoximes.—The method of
hydrolysis employed varied considerably according to the nature
of the product to be identified. In the cases of picryl-*o*-, *m*-, and
p-nitrobenz*syn*aldoximes, the finely-powdered compound (2 g.) was
suspended in $2N$-sodium hydroxide (45 c.c.) for some time (ortho,
15 hours; meta, 6 hours; para, 48 hours) and the solution was
then filtered. The solid residue was identified, after crystallisation
if necessary, as the corresponding nitrile by the method of mixed
melting points. The filtrate was shaken with concentrated potass-
ium carbonate solution, the potassium picrate, which separated in
characteristic silky needles, was decomposed with acid, and the
picric acid identified. Picryl-3 : 4-methylenedioxybenz*syn*aldoxime
(0.5 g.) was warmed for 3 minutes with 5% alcoholic sodium
hydroxide (25 c.c.), diluted with water (50 c.c.), and left over-

night. The solid which had crystallised was identified as 3 : 4-methylenedioxybenzonitrile, and picric acid was identified in the solution.   Picrylbenz*syn*aldoxime and picrylcinnam*syn*aldoxime were treated similarly, except that the liquid nitriles, obtained by extracting the diluted alcoholic solution with ether, were hydrolysed and the benzoic and cinnamic acids identified.   Picryl-*p*-methoxy-benz*syn*aldoxime (2 g.) was heated on the water-bath for 30 minutes with 2*N*-sodium hydroxide (35 c.c.), when a red solution was obtained and ammonia was evolved.   Hydrochloric acid was added and, after cooling, the precipitate was collected and washed with cold water until the washings were no longer yellow.   The residue was *p*-methoxybenzoic acid, and picric acid was isolated from the filtrate.   *o*-Methoxybenzoic acid could not be separated from picric acid satisfactorily, so picryl-*o*-methoxybenz*syn*aldoxime (0·5 g.) was heated on the water-bath with 2*N*-sodium hydroxide (30 c.c.). Decomposition occurred slowly and oily drops appeared on the surface.   The liquid was cooled and the oil removed with ether and subsequently hydrolysed with sodium hydroxide, when ammonia and *o*-methoxybenzoic acid were obtained, indicating that the oil was the nitrile.   When picryl-*p*-dimethylaminobenz*syn*aldoxime was similarly treated, the oil solidified and was identified as *p*-dimethylaminobenzonitrile.   Picryl - 3 - methoxy - 4 - picryloxybenz*syn*-aldoxime (0·5 g.) was heated for 2—3 minutes with 5% alcoholic potassium hydroxide, the solution diluted and saturated with carbon dioxide; after keeping over-night, potassium picrate separated, and chloroform extracted 3-methoxy-4-hydroxybenzo-nitrile from the solution.

Acid Hydrolysis of Picrylbenzsynaldoximes.—In the cases of picryl-*p*-methoxy-, 3 : 4-methylenedioxy-, and *p*-nitro-benz*syn*-aldoximes, the picryl compound was heated on the water-bath under reflux with concentrated hydrochloric acid for 6 hours.   On cooling, picric acid and the corresponding benzoic acid crystallised out.   The solid was washed with cold water until the washings were no longer yellow, and the residue identified as the correspond-ing benzoic acid.   Very little *o*-nitrobenzoic acid was obtained owing to its solubility in water being similar to that of picric acid, whilst with picryl-*m*-nitrobenz*syn*aldoxime it was found impossible to separate satisfactorily the two acids produced.   In the cases of picrylbenz*syn*aldoxime and picrylcinnam*syn*aldoxime, the acids were separated by steam distillation.   When picryl-*o*-methoxybenz*syn*aldoxime was hydrolysed in this way, very little solid separated, so the solution was extracted with ether; the material thus removed, after crystallisation from water, was found to be salicylic acid, formed by the elimination of the methyl group

as methyl chloride. From the hydrolysis of picryl-*p*-dimethyl-aminobenz*syn*aldoxime only picric acid separated; this was removed and the filtrate made faintly alkaline with sodium hydroxide, when the cautious addition of dilute acetic acid precipitated *p*-di-methylaminobenzoic acid. Picryl-3-methoxy-4-picryloxybenz*syn*-aldoxime could not be hydrolysed under the above conditions.

Action of Picryl Chloride on syn*Aldoximes.*—*p*-Methoxybenz*syn*-aldoxime (2·5 g.) was dissolved by very gentle warming in alcohol (30 c.c.), and a solution of sodium ethoxide (0·38 g. of sodium in 10 c.c. of alcohol) added, followed by a warm solution of picryl chloride (4·13 g.) in alcohol (40 c.c.). An evanescent wine-red coloration developed changing to a dirty yellowish-brown with the deposition of a small amount of sodium chloride which was free from organic matter. The liquid after dilution was distilled in steam, the first portion passing over rich in alcohol being collected separately. From the second portion white crystals of *p*-methoxy-benzonitrile separated; after drying in a vacuum, 0·8 g. was obtained corresponding to 36% yield. The filtrate from these was treated with semicarbazide hydrochloride and sodium acetate, whereupon, on stirring and keeping, *p*-methoxybenzaldehydesemi-carbazone (0·66 g.) crystallised, identified by the method of mixed melting points. The alcoholic portion of the distillate gave no precipitate on dilution, but on treatment with semicarbazide hydrochloride and sodium acetate and concentrating gave a further 0·17 g. of the semicarbazone, making a total yield of 26% of aldehyde. Picric acid was isolated from the liquid in the distilling flask after removal of tar. Similar results were obtained using benz*syn*aldoxime, cinnam*syn*aldoxime, and hept*syn*aldoxime, except that in these cases the nitrile, being liquid at room temperature, did not separate. The whole of the distillate was accordingly treated with semicarbazide hydrochloride and sodium acetate, the semicarbazone separated, and the mother-liquor extracted with chloroform. After removing the solvent, the nitrile was hydrolysed with concentrated hydrochloric acid in the case of the benzonitrile, with 50% sulphuric acid in that of cinnamonitrile, and with 50% potassium hydroxide in the case of heptonitrile, and the acids were identified. The yield of aldehyde, weighed as semicarbazone, was: benzaldehyde 33%, cinnamaldehyde 28%, and heptaldehyde 24%.

Further Investigation of the Action of 2 : 4-*Dinitrochlorobenzene on* syn*Aldoximes* (Compare Brady and Truszkowski, *loc. cit.*).—The action of 2 : 4-dinitrochlorobenzene on *p*-methoxybenz*syn*aldoxime has been again investigated, but no indication of the formation of nitrile was obtained, thus confirming the earlier observation.

The action of 2 : 4-dinitrochlorobenzene on hept*syn*aldoxime has

also been investigated more fully, this compound being selected as a readily purified, stable *syn*aldoxime. A solution of 1·069 g. of sodium in 25 c.c. of absolute alcohol was mixed with one of 5·996 g. of hept*syn*aldoxime in 35 c.c. of absolute alcohol, and 9·412 g. of dinitrochlorobenzene in 35 c.c. of warm absolute alcohol were added. The mixture was left over-night in a corked flask, filtered, and the precipitate washed with a little absolute alcohol. The precipitate after drying in a vacuum over calcium chloride weighed 1·89 g.; it was dissolved in water and the brown solution made up to 100 c.c. A part was tested for hydroxylamine with negative results, whilst in another portion, acidified with nitric acid, the ionisable chlorine was determined by Volhard's method. The amount found indicated 59·4% chlorine in the solid, which apparently consisted of sodium chloride with a little highly-coloured impurity (NaCl contains 60·7% Cl). The filtrate from this solid was strongly acid to litmus. A portion was made strongly alkaline with sodium hydroxide to fix any unchanged oxime and extracted with chloroform to remove aldehyde, etc. The alkaline aqueous layer was treated with sufficient ammonium chloride to decompose the whole of the sodium hydroxide added and again extracted with chloroform, when a very small amount of hept*syn*aldoxime was obtained. The rest of the filtrate was distilled in steam to remove heptaldehyde. The liquid in the flask was heated with the addition of concentrated hydrochloric acid to induce if possible the hydrolysis of any β-dinitrophenylhydroxylamine, made alkaline with sodium hydroxide, and again distilled in steam; ammonia but not hydroxylamine could be detected in the distillate. The disappearance of the hydroxylamine does not seem to be due to the subsequent treatment of the mixture, since aldehyde is produced immediately (see action on acetaldoxime below), and it has been found that aldehyde cannot be distilled in steam even from a mixture of equimolecular quantities of heptaldehyde and hydroxylamine hydrochloride in water. Hydroxylamine can decompose according to the equation $3NH_2 \cdot OH \longrightarrow NH_3 + N_2 + 3H_2O$, but it has been found that hydroxylamine can be distilled in steam practically quantitatively from an aqueous solution of hydroxylamine hydrochloride with two molecular proportions of sodium hydroxide. On the other hand, when 2 : 4-dinitrophenol, hydroxylamine hydrochloride, and excess of aqueous sodium hydroxide were distilled in steam, no hydroxylamine was obtained, but ammonia was detected, the amount being 92% of that demanded by the above equation. Under similar conditions, dinitrophenol and sodium hydroxide gave only a trace of ammonia. Dinitrophenol does not, however, decompose hept*syn*aldoxime in alkaline

solution. The difficulty in accepting the above method of decomposition of the hydroxylamine in the actual reaction is that no gas is evolved. As a result of these experiments, it seems that an *N*-dinitrophenyl derivative is first formed which immediately decomposes, the hydroxylamino-residue remaining attached to the dinitrophenyl radical; the β-dinitrophenylhydroxylamine then decomposes in such a way that no hydroxylamine is formed. An attempt was made to isolate these products of decomposition employing acet*syn*aldoxime, which has the advantage that the aldehyde formed is soluble in water. Acetaldoxime (12 g.) in alcohol (12 c.c.) was added to a solution of sodium (4·6 g.) in alcohol (100 c.c.), and a warm solution of 2 : 4-dinitrochlorobenzene (40·5 g.) in alcohol (150 c.c.) added. The liquid immediately turned dark brown and torrents of acetaldehyde were evolved. After cooling, the precipitate was found to consist of sodium chloride and some sodium dinitrophenoxide. On diluting the filtrate and leaving, a considerable amount of tar separated from which the only compound that could be isolated was a small quantity of dinitrochlorobenzene. From the mother-liquor small amounts of dinitrochlorobenzene and dinitrophenol were obtained. It seems, therefore, unlikely that the β-dinitrophenylhydroxylamine decomposed in the manner described for β-dinitrotolylhydroxylamine by Anschutz and Zimmermann (*Ber.*, 1915, **48**, 152),

$$3(NO_2)_2C_6H_2Me \cdot NH \cdot OH \longrightarrow (NO_2)_2C_6H_2Me \cdot NH_2 +$$
$$(NO_2)_2C_6H_2Me \cdot \underset{O}{N \cdot N} \cdot C_6H_2Me(NO_2)_2 + 2H_2O,$$
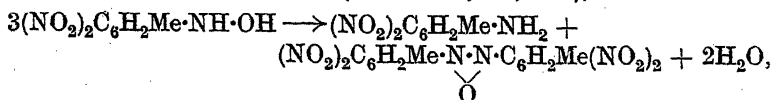
as it should not have been difficult to isolate the sparingly soluble, high-melting amine or azoxy-compound. The alternative rearrangement
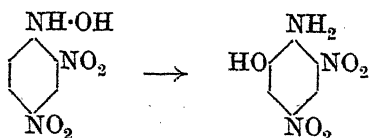
is unlikely and would not hold for the trinitro-compound. The only alternative therefore appears to be that the hydroxylamino-group is decomposed at the expense of the rest of the molecule, a view supported by the decomposition of hydroxylamine by dinitrophenol in the presence of alkali.

Fusion Diagram of the Cinnamaldoximes with
2 : 4-Dinitrochlorobenzene.

This was constructed in the usual manner, the freezing points being obtained from cooling curves. It was found impossible to

use a mixture containing more than 60% of the oxime owing to decomposition during melting. The results are given in Table I.

TABLE I.

Mol. % of cinnam*anti*ald-oxime.	F. p.	Eutectic.	Mol. % of cinnam*syn*ald-oxime.	F. p.	Eutectic.
0	48·8°		0	48·8°	
3·3	47·3		2·7	47·5	
6·4	49·8	47·1°	5·2	47·2	46·5°
19·4	60·5		7·6	46·8	46·8
21·6	62·6		9·9	48·8	46·6
25·7	64·2		21·6	61·0	
40·8	68·7		35·5	68·3	
50	69·6		45·2	69·2	
53·4	68·9		50	69·4	
57·9	67·5		52·4	69·3	
			58	68·1	

The maximum in each case (69·6°, 69·4°) corresponds to a compound of equimolecular quantities of dinitrochlorobenzene and the oxime, and in this neighbourhood the curves follow each other closely. When equimolecular quantities of each oxime and of dinitrochlorobenzene were melted together and the products mixed, the freezing point of this mixture was 69·6°. Each compound was ground for a few minutes with cold 2*N*-sodium hydroxide; the insoluble residue was dinitrochlorobenzene, whilst the solution on being saturated with carbon dioxide gave in each case cinnam-*anti*aldoxime. There seems, therefore, little doubt that the two substances are identical.

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CXX.—*The Equilibria Underlying the Soap-boiling Processes. Pure Sodium Palmitate.*

By JAMES WILLIAM McBAIN and GUY MONTAGUE LANGDON.

THE processes of soap boiling depend upon the existence of a series of well-defined equilibria, which have, however, received very little systematic study. The present contribution records observations upon equilibria in nearly two hundred systems containing pure sodium palmitate, water and sodium chloride over a range of temperature up to about 200° (in sealed tubes). Most of the work here recorded was completed in 1922 and the theoretical treatment in the previous communication by McBain and Burnett (J., 1922, **121,** 1320) was based upon a knowledge of these unpublished

results. Many of the systems were preserved and have now been re-examined together with fresh specimens. Their behaviour appears to be independent of time.

It is now possible to deal fairly simply with the various forms in which soap and its solutions occur. Probably every soap can be prepared in each of the two solid microcrystalline forms; namely, hexagonal plates and curd fibres. The hexagonal form may be dismissed for the present purpose, since it is only a transient, unstable form of sodium soap. The curd fibres contain water as well as traces of salt, and are characterised by their fineness. This involves a very large exposed surface, which makes it difficult to determine the relative amounts of chemically combined and sorbed water,* but it is certain that the hydration of the curd fibres depends upon the composition of the mother-liquor out of which they crystallised.

There are three forms of soap solution proper, all of them transparent, two are anisotropic or doubly refracting, and the third is isotropic, that is, dark when examined between crossed Nicols. These three forms of transparent solutions will be referred to as " neat soap," " middle soap," and " isotropic solution." All these are separate phases, mutually immiscible. Dr. K. Maclennan of Port Sunlight (*J. Soc. Chem. Ind.*, 1923, **42**, 3937) has rendered valuable service in directing attention to the importance of anisotropic plastic liquids in the soap-boiling processes. We find that every soap solution in sufficiently high concentration is anisotropic (doubly refracting, " liquid crystal," " mesomorphic "). This property is not confined to any one concentration, but extends over a wide range of composition even to concentrated soap solutions containing a certain amount of salt.

These remarkable solutions are clear, transparent, plastic masses which readily flow under their own weight when prepared in quantity as in the soap pan. Small specimens retain their shape indefinitely and look like pieces of clear, stiff jelly, from which, however, they differ fundamentally. A jelly is highly elastic and when not under strain is isotropic, whereas these anisotropic liquids are always doubly refracting and are largely devoid of elasticity. For instance, if a small portion of the surface of a specimen of $3N_w$(weight normal)-potassium laurate is pulled up into a sharp point with a glass rod, the projecting tongue retains its form and position apparently unchanged even after 10 years, but if jarred, assumes new positions under the stress and, if again undisturbed, retains these new forms indefinitely. In other words, the flow is plastic, not elastic or

* For previous communications on this subject, see J., 1919, **115**, 1300; 1921, **119**, 1369, 1669, 1374; 1924, **125**, 1971.

viscous, and there is no relaxation under a small force applied for a long time.

We have established that anisotropic and isotropic soap solutions constitute separate immiscible phases. Dissolution of the clear plastic anisotropic liquid in water requires time even with vigorous stirring. Their separate existence in different ranges of concentrations and their immiscibility has been substantiated in this laboratory by W. J. Elford for potassium laurate, by F. Maggs for potassium oleate, by H. M. Kamil for sodium abietate, by D. P. Davies for sodium ricinoleate, and by Miss E. M. Grant for potassium laurate at high temperatures (all unpublished).

One of the two anisotropic forms, "neat soap," is familiar to all soap-boilers, because most good household soaps are derived from it. It is a homogeneous, plastic liquid at the boiling point which forms the upper layer in the soap pan or kettle in the fitting, settling, or pitching process and it is characterised in industry by its content of about 63% of fatty acid for sodium soaps and about 40% of fatty acid for potassium soaps. The commercial neat soap, however, is but one particular case, and we have followed the continuous field of existence of this phase back to pure aqueous solutions of the salt of one fatty acid and up to pure molten anhydrous sodium soap.

The existence of the other anisotropic soap which occurs in medium concentrations and which we therefore call " middle soap " has been hitherto unsuspected, although it will become evident from the position of its field of existence that it may play an important and disturbing rôle both in the manufacture and in the use of soap preparations. It appears to be a conic anistropic liquid (McBain, Nature, 1924, 114, 49; see there photograph by W. J. Elford).

The boundary between " middle soap " and " neat soap " has not yet been sufficiently elucidated owing to experimental difficulties which are only now being overcome. It is certain that they are separate, immiscible phases at higher temperatures, and it is probable that they remain so even at the lowest temperatures.

There is a wide range of soap solutions, with and without added salt, all of which are isotropic, not lighting up the field between crossed Nicols. This range extends continuously from pure water up to a definite limiting concentration of soap, which limit is even higher when salt is added. Within this continuous field the viscosity and other properties of the soap solutions vary greatly, and in the parts of the field representing the higher concentrations of soap, and those to which an optimum amount of salt has been added, the solutions often assume the form of true elastic transparent jellies which are, of course, isotropic. The part of this field where the solutions contain much salt and but little soap includes the

thin " lyes " of the soap pan or kettle, whereas the solutions containing more soap and a fairly large amount of salt include the " nigre " * the separation of which from the " neat soap " layer constitutes the final stage of the soap-boiling processes. These isotropic soap solutions cover an extremely wide range at very high temperatures. Above 316°, for example, sodium palmitate is an isotropic liquid miscible in all proportions with water or salt solutions.

This simple formulation of the possible forms in which soap may appear, which has required so many years of study for its elucidation, reduces the experimental problem merely to a determination of the limiting concentrations which bound the isotropic and anisotropic fields, respectively. The variations in the third possible phase— the curd fibres—are relatively small, although they merit further detailed investigation, because these fibres are the main constituent of household soap.

The present paper, then, consists essentially of a delimitation of the ranges of concentration of the two forms of soap solution together with an indication of the phases which can co-exist in equilibrium. The results are of general significance, for all the typical equilibria of the soap-boiling processes (silicates apart) are to be found in soap systems prepared from a single fatty acid. Futhermore, all sodium and potassium soaps, pure or commercial, exhibit the same type of equilibria, differing only in the exact concentrations at which the various phases appear.

EXPERIMENTAL.

Method.—The method of examination has been partly described in the previous communication with Burnett. It rests upon the principle that supersaturation does not occur in regard to the appearance of a liquid phase, a direct deduction from the kinetic theory.† It is our experience that this is likewise true of both forms of the anisotropic liquid—which distinguishes them significantly from crystalline phases. On cooling the homogeneous solution to its critical temperature, droplets of anisotropic liquid promptly appear, and on rewarming with efficient stirring the emulsion becomes homogeneous at exactly the same temperature. The phenomenon is thus independent of time or of the direction from which it is approached, provided that the stirring is really efficient.

* So-called because colouring matters go into this layer, making it dark brown.

† Crystallisation to form curd fibres, on the contrary, usually occurs only after at least four or five degrees of undercooling.

This visual observation is confirmed and rendered much more precise by examination between crossed Nicols whenever the liquid appearing or disappearing is anisotropic. The temperature at which the contents of the sealed tube become completely isotropic and dark between crossed Nicols is the same as the temperature at which the mixture becomes homogeneous on warming and stirring.* As the temperature is lowered, the degree of anisotropy is observed to increase, but it is impossible to follow quantitatively the extent to which isotropic liquid is replaced by anisotropic liquid with this form of examination in a large sealed tube immersed in a thermostat at high temperature, or to determine the temperature at which the transformation is complete. This is only possible with a thin section under a microscope using a solution appreciably below its boiling point. None of these solutions boils at a temperature more than a few degrees above 100°, but they can be studied in sealed tubes up to a temperature of several hundred degrees.

Determination of the solubility of curd fibres of soap resolves itself into an observation of the temperature at which, with efficient stirring, the last curd fibre just dissolves. A useful check in determinations with very cloudy concentrated solutions is suddenly to chill the specimen when the curd is thought to have melted; a pronounced change in appearance shows that curd had dissolved. This test is very distinct and defines the " melting point " within a degree. For the systems to be discussed in the present paper, sodium palmitate at room temperature is nearly insoluble and addition of salt reduces its solubility still further, so that all systems consist of opaque, white masses of crystalline curd fibres of hydrated soap enmeshing the remaining liquid which is practically devoid of soap (see, for example, Laing and McBain, J., 1920, 117, 1525). The equilibrium or phase-rule diagram at room temperature consists of a short line at the top representing composition of the curd fibres and a long line at the bottom representing aqueous salt solutions containing traces of sodium palmitate. The only possible systems at room temperature are mixtures of curd fibres with this salt lye in various proportions.

With rise of temperature, the solubility of the curd fibres increases enormously so that a $1 \cdot 0 N_w$-solution of soap is in completely homogeneous solution at 67°. The general form of these equilibria and the effect of salt can be deduced from the data for sodium laurate in the previous communication. The present paper is concerned with the equilibria at high temperatures, and all that it is necessary to remember is that below about 70° the anisotropic liquid com-

* If stirring is avoided the layers with a mirror-like surface are preserved up to temperatures far above the critical.

pletely disappears owing to the formation of curd fibres. It is easy, however, to get a suspended transformation at much lower temperatures.

Materials.—It is difficult to obtain large samples of sodium palmitate of sufficient purity to lend themselves to the present purpose. Most commercially pure sodium palmitates yield deep brown solutions; although if pure, even highly concentrated solutions should be colourless. On keeping at 150° for a day or two, concentrated solutions gradually darken. For the preliminary work, specially that dealing with low concentrations and equilibria between nigre and lye, a specially made specimen of English origin was used, although from analysis it contained some stearate. The later work was carried out with two specimens made by Kahlbaum, although neither of these was nearly as good, either in neutrality or colour, as solutions made by ourselves from sodium drippings and palmitic acid "Kahlbaum." The first Kahlbaum specimen was distinctly alkaline, 1 g. containing 0·0012 g. of sodium hydroxide (*i.e.*, 0·9 equivalent % excess of alkali). This is almost enough to salt out the soap in very highly concentrated solution. Kahlbaum's second specimen was nearly neutral, containing only 0·1 equivalent % excess of alkali. This was used for nearly all experiments in high concentration. To harmonise the results given by the first specimen for temperatures of appearance of two liquid layers with those obtained with the Kahlbaum material, 40° was subtracted from the former observations and the data recorded include this correction. It may be recalled that the colour accumulates in the nigre, the anisotropic " neat soap " being very much paler.

The solutions were made up in sealed evacuated tubes with boiled-out, distilled water. " A.R." or " Kahlbaum's purest sodium chloride " was used. Owing to the extreme viscosity or plasticity of the materials, the contents of a number of the tubes never became thoroughly mixed and such experiments were discarded. Concentrations are expressed in weight normality (gram-equivalents per kilo. of water); in " fractions " (1 gram-equivalent of sodium palmitate, 1 gram-equivalent of salt, and 1 kilo. of water, each being taken as unity; thus a solution which is weight normal with regard to sodium palmitate as well as to salt is 0·333 sodium palmitate, 0·333 salt, and 0·333 water); and in technical units, namely, percentage of fatty acid and of salt in 100 parts of water by weight of the mixture (thus the solution just described is 19·2% fatty acid and 4·4% salt).

Applicability of the Phase Rule.

It is our experience that the properties of a soap solution are completely determined by its composition and temperature, and

it is evident that the equilibria within the solution are defined to within about 1%. In the previous communication, the view was advanced that from the standpoint of the phase rule such a colloidal solution behaves as a single phase towards external equilibria with other phases. This suggestion that the phase rule is directly applicable is borne out by all our observations; in fact, only eight tubes out of nearly a thousand studied have suggested even a slightly discrepant behaviour; these will be discussed later. Even if these slight divergences are substantiated, the phase rule constitutes an excellent description of the equilibria involving soap solutions and the soap-boiling processes. Indeed, the equilibria in soaps of mixed commercial oils and fats (apart from the formation of curd) closely resemble those of a three-component system such as that derived from a single pure soap, a single salt and water.

In the three-component system sodium palmitate–sodium chloride–water there is one degree of freedom if, in addition to vapour, two other phases are present, and the temperature is fixed. That is to say, if both phases can vary in composition, they must do so in dependence upon each other, and it is only when three phases are present in addition to vapour that the compositions of those phases are completely fixed for any definite temperature. At a given temperature, such as the boiling point, the commonly occurring equilibria involve two liquids, or a liquid and a solid (curd fibres). In the soap pan, the usual equilibria are (a) anisotropic liquid, " neat soap," with isotropic liquid, " nigre," (b) anisotropic liquid soap with isotropic liquid lye, and (c) the more complicated equilibria involved in graining out, where, in addition to anisotropic liquid soap and liquid lye, curd fibres of the soaps of the more insoluble fatty acids progressively separate out. In soap-boiling practice, owing to the mixture of highly soluble with the more insoluble soaps, there is never sufficient salt added completely to grain out the whole of these soaps as curd fibres.* Equilibria between (d) isotropic nigre and isotropic lye occur in solutions much too dilute to appear in the soap pan; and the equilibria between (e) an isotropic soap and curd fibres in the absence of lye occur only in concentrations above those used in the soap pan, but they occur when neat soap is cooled in the frames.

Analysis of the Separate Layers.—Systems in which three liquid layers occur should exist at only one temperature whenever the total composition of the system is fixed. However, eight instances were met with in which three layers seemed to persist over a range of temperatures of 10° to 40°. The three layers involved were neat soap, nigre and lye. The total composition of the system approxi-

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* This point was not made clear in the Fourth Colloid Report.

mated in each case to that of nigre. This slight, but distinct deviation from the requirements of the phase rule is not due to hydrolysis, but might well be due to a lag in the establishment of the internal equilibria. It is certainly due in part to the difficulty of thoroughly mixing and then separating the most viscous layer. In any case, 30° is only a small fraction of the range of temperature over which the equilibria have been studied and the phenomenon is confined to one small part of the diagram, namely, that where the nigre contains its maximum amount of salt. It was met with, for example, in tubes in which the sodium palmitate was 0·605, 0·608, 1·009, and 0·383N_w, respectively, and the sodium chloride 1·440, 1·30, 1·465, and 1·504N_w, respectively. The second instance is particularly interesting, as it apparently occurs at the exact point at which, on heating at 141°, three layers are converted into one homogeneous layer and the discrepancy in all cases consists in the persistence of the middle layer at temperatures appreciably below this. Thörl and Bätz (see later) obtained three layers in most of their experiments, but they worked at a constant temperature and the composition of each of their three phases was constant almost within the error of experiment.

Table I contains the results of analyses of the separate layers of a few tubes, the first four of which exhibited the persistence of three layers over a temperature range of about 30°. All the analyses show the high degree of entanglement of the middle layer in the plastic upper layer of neat soap, and the analysis of the middle layer in the first tube showed that it included large amounts of the upper layer. The lye contains only negligible amounts of sodium palmitate and separates completely from nigre. Before analysis, the tube containing the system was heated with occasional shaking at 90° for several days, then suddenly chilled, and opened for analysis. Water was calculated by difference.

TABLE I.

Weight normalities (N_w) of soap and salt in liquid phases co-existing at 90°.

No.	Neat soap.		Nigre.		Lye.	Total system.	
	NaP.	NaCl.	NaP.	NaCl.	NaCl.	NaP.	NaCl.
1	3·45	0·89	2·41	1·01	0·96	1·40	0·93
2	2·91	0·83	0·65	1·11	1·06	1·42	0·89
3	2·88	0·73	0·54	1·15	0·99	1·30	0·94
4	2·94	0·75	0·61	1·10	1·08	1·18	0·93
5	3·83	0·57	2·80	0·63	—	2·87	0·48
6	3·33	0·66	1·56	0·71	—	2·49	0·55
7	3·36	0·87	0·85	0·90	—	1·50	0·83
8	2·53	0·91	—	—	1·17	0·606	1·15
9	—	—	0·377	0·98	1·02	0·296	0·98

TABLE II.

Solubility of curd fibres of sodium palmitate as shown by the minimum temperature (T) at which they just completely dissolve to form one homogeneous liquid.

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
10·0 (K)	0·9091	65·3	—	—	—	(90°)
1·009	0·5022	19·5	—	—	—	67
0·504	0·3354	10·9	—	—	—	63
3·018	0·6998	40·1	0·2935	0·0682	0·92	(77)
1·008	0·3745	18·8	0·680	0·2531	3·01	76
0·5044	0·2194	10·5	0·7943	0·3455	3·91	74*
0·504	0·2457	10·6	0·55	0·2668	2·74	72
0·504	0·2348	10·6	0·642	0·2991	3·19	76
0·503	0·2245	10·5	0·738	0·3295	3·65	75·5
0·3987 (K)	0·1730	8·5	0·9065	0·3933	4·55	76
0·3515	0·1608	7·5	0·8347	0·3818	4·46	75
0·2063	0·1010	6·0	0·8358	0·4094	4·35	74
0·1353	0·0692	3·1	0·8189	0·4191	4·41	72·5
0·06096	0·0326	1·4	0·8067	0·4319	4·43	72·5
0·0583	0·0297	1·3	0·9082	0·4618	4·97	(75)

K = Kahlbaum's sodium palmitate.

* On undercooling, two layers formed at about 30°.

TABLE III.

Temperatures (T) at which, upon cooling, a single liquid soap solution separates into two liquid layers both isotropic (nigre and lye).

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
1·297	0·4009	22·7	0·9396	0·2903	3·88	98°
1·180	0·3793	21·1	0·9303	0·2991	3·93	92·5
1·000	0·3335	18·5	0·9984	0·3330	4·37	98
0·8610	0·3006	16·4	1·003	0·3501	4·51	88
0·7776	0·2799	15·1	1·001	0·3601	4·59	92
0·6947	0·2502	13·7	1·081	0·3896	5·03	95
0·6061	0·2196	12·2	1·155	0·4185	5·46	119
0·5669	0·1968	11·4	1·277	0·4490	6·06	145
0·5659	0·2203	11·5	1·003	0·3904	4·82	80
0·5425	0·2005	11·0	1·163	0·4299	5·58	115
0·4944	0·1950	10·2	1·042	0·4110	5·08	84
0·4613	0·1782	9·5	1·127	0·4353	5·51	85
0·4455	0·1797	9·3	1·034	0·4170	5·10	78
0·4180	0·1601	8·7	1·194	0·4572	5·89	125
0·3810	0·1604	8·1	0·9942	0·4187	4·99	84
0·3405	0·1376	7·2	1·133	0·4580	5·70	121
0·2960	0·1300	6·5	0·9797	0·4303	5·02	90
0·2842	0·1287	6·2	0·9234	0·4184	4·77	60
0·2782	0·1193	6·1	1·052	0·4516	6·40	123
0·2018	0·0907	4·4	1·022	0·4594	5·35	95·5
0·1981	0·0889	4·4	1·029	0·4620	5·40	88
0·1054	0·0502	2·4	0·9883	0·474	5·32 above 143	
0·1001	0·0502	2·4	0·8930	0·4480	4·83	94
0·0997	0·0502	2·6	0·8851	0·4459	4·79	71
0·0279	0·0143	0·7	0·9317	0·4753	5·12	85
0·0202	0·0098	0·5	1·046	0·5060	6·11	141

TABLE IV.

Temperatures (T) at which, upon cooling, a single isotropic liquid soap solution separates into two liquid layers, isotropic nigre and anisotropic neat soap.

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A.	N_w.	Fraction.	% salt.	T.
6·58	0·8506	57·2	0·154	0·0199	0·32	above 155°
5·46	0·8198	53·3	0·1995	0·0300	0·46	„ 160
4·87	0·7632	50·5	0·514	0·0804	1·26	„ 161
4·135	0·7394	46·9	0·4583	0·0820	1·23	„ (153)
4·131	0·7401	46·9	0·4523	0·0810	1·21	„ (160)
4·054	0·7782	46·1	0·1562	0·0300	0·43	(150)
3·975	0·7911	46·6	0·0497	0·0099	0·14	above 150
3·508	0·6993	43·2	0·5084	0·1014	1·48	„ (155)
3·389	0·7492	42·1	0·1348	0·0298	0·40	143
3·284	0·7396	42·1	0·1558	0·0351	0·47	81
3·185	0·7303	42·4	0·1775	0·041	0·55	74
3·126	0·7199	41·0	0·2158	0·0497	0·67	78
3·082	0·7169	40·6	0·2175	0·0506	0·68	80
2·976	0·6987	39·8	0·2775	0·0652	0·88	86
2·871	0·6594	38·9	0·4833	0·1110	1·55	above 158
2·818	0·7088	38·8	0·2040	0·0507	0·66	62
2·808	0·6634	38·9	0·4250	0·1004	1·36	145
2·702	0·6784	37·7	0·2805	0·0704	0·93	70
2·700	0·6717	37·7	0·3223	0·0801	1·06	76
2·653	0·6615	37·2	0·3572	0·0891	1·20	82
2·586	0·6492	36·7	0·3997	0·1001	1·34	85
2·486	0·6167	35·7	0·5459	0·1354	1·85	127
2·007	0·5423	31·0	0·694	0·1875	2·54	82·5
2·007	0·5594	31·1	0·5801	0·1617	2·13	46
1·958	0·5495	30·6	0·6049	0·1698	2·24	86
1·500	0·4502	25·3	0·8305	0·2494	3·31	92·5
1·492	0·4550	25·2	0·7875	0·2401	3·15	61
1·464	0·4480	24·9	0·8064	0·2461	3·21	61
1·417	0·4285	26·0	0·8900	0·2692	3·60	95·5
1·403	0·4207	24·0	0·9326	0·2796	3·37	104
1·374	0·4505	23·8	0·6758	0·2215	2·78	41
1·297	0·4009	22·7	0·9396	0·2903	3·88	98
1·290	0·4002	22·5	0·9333	0·2896	3·86	80
1·214	0·3954	21·6	0·859	0·2796	3·62	57
1·180	0·3793	21·1	0·9303	0·2991	3·93	92·5
1·03	0·3387	18·8	1·013	0·3328	4·40	88·5
1·021	0·3583	18·9	0·829	0·2908	3·64	46
1·014	0·3523	18·8	0·865	0·3005	3·80	49
1·009	0·3271	18·5	1·075	0·3485	4·68	91
1·001	0·3649	18·7	0·742	0·2705	3·28	37
0·7415	0·2655	14·4	1·042	0·3744	4·80	86
0·7409	0·2694	14·2	1·008	0·3667	4·66	54
0·6682	0·2598	13·3	0·9033	0·3513	4·26	41
0·666	0·3298	13·4	0·760	0·2894	3·61	32
0·6634	0·2353	13·1	1·157	0·4102	5·40	95
0·6582	0·2324	13·0	1·174	0·4145	5·50	98
0·608*	0·2084	12·1	1·30	0·4485	6·10	141
0·5456	0·2017	11·0	1·160	0·4285	5·56	91·5
0·503	0·2003	10·2	1·008	0·4015	4·90	64
0·503	0·2116	10·4	0·874	0·4207	4·29	37

* Formed three layers, two disappearing at about the same temperature.

TABLE V.

Temperatures (T) at which, upon cooling, a single liquid soap
solution separates into two liquid layers, one isotropic and the
other anisotropic ("middle soap").

Sodium palmitate.			Sodium chloride.			
N_w.	Fraction.	% F.A	N_w.	Fraction.	% salt.	T.
0·2952	0·7469	40·0			—	155·
1·991	0·6657	31·6			—	141
1·683	0·6273	28·4			—	123
1·454	0·593	25·6			—	97
1·363	0·5768	24·4			—	87
1·277	0·5610	23·2			—	80
1·009	0·5022	19·5			—	65
3·389	0·7492	42·9	0·1348	0·0298	0·40	143
3·284	0·7396	42·1	0·1558	0·0351	0·47	81
3·263	0·7510	42·1	0·0872	0·0200	0·26	130
2·855	0·7188	39·2	0·1184	0·0298	0·44	140
2·843	0·7101	39·1	0·1618	0·0404	0·53	119
2·818	0·7088	38·8	0·2040	0·0507	0·66	62
2·811	0·7006	38·7	0·2020	0·0503	0·66	66
2·777	0·6911	38·4	0·242	0·0604	0·79	above 63
2·771	0·6908	38·3	0·2414	0·0602	0·79	80
2·513	0·6797	36·3	0·1841	0·0498	0·63	122
2·435	0·6600	35·5	0·256	0·0694	0·88	66
2·356	0·6598	34·9	0·2135	0·0598	0·75	103
2·235	0·6694	34·0	0·1024	0·0306	0·37	146
2·191	0·6412	33·4	0·2252	0·0660	0·81	93
2·150	0·6489	33·0	0·1645	0·0497	0·60	125
1·868	0·6190	30·2	0·1508	0·0500	0·57	121
1·728	0·6088	28·7	0·1104	0·0389	0·44	106
1·561	0·5974	26·8	0·0525	0·0201	0·21	98

Experimental Data.—Temperatures at which curd fibres com-
pletely dissolved to form homogeneous liquid or anisotropic liquid
are collected in the last column of Table II. The composition
recorded is the solubility of sodium palmitate at that temperature
and it is seen that the solubility depends upon the amount of salt
present. The first three columns give the concentration of sodium
palmitate and the second three of sodium chloride in weight nor-
malities, modified molar "fractions," and technical units, respec-
tively. In the two cases indicated, where the formation of curd
on cooling was suspended, two liquid layers were formed at a lower
temperature. Two degrees have been subtracted from the results
obtained with sodium palmitate other than Kahlbaum.

In Table III are collected the observations upon systems which
are homogeneous, isotropic liquids at high temperatures and, on
cooling, separate into two liquid layers both of which are isotropic
(nigre and lye).

In Table IV are collected the observations upon solutions which
at very high temperatures are homogeneous and isotropic but which
on cooling separate into two liquid layers, one isotropic and the

other anisotropic. These pairs correspond to the soap boiler's nigre and neat soap, respectively. In many instances, owing to the consistency of the plastic liquid, the two phases did not separate into two distinct layers but remained coarsely emulsified.

Discussion of Results.

The work carried out in this laboratory clearly establishes for the first time the general properties of the whole of the phase-rule diagram for soaps with and without salt. Many quantitative

FIG. 1.
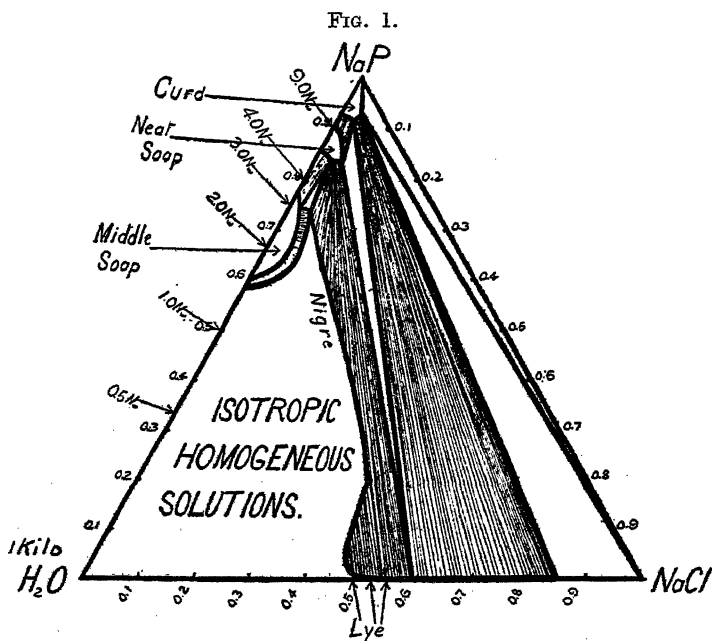
Phase rule diagram at 90°, concentrations being expressed in fractions of mols. of sodium palmitate and sodium chloride, but in fractions of one kilogram for water. The shaded areas represent the approximate direction of the tie lines in the two-layer systems.

measurements remain to be carried out, but the largest part of the diagram, that involving isotropic solutions, has been accurately mapped and the nature and the approximate composition of the phases in equilibrium with them have been determined. The results are best discussed with reference to the accompanying diagrams.

Fig. 1 represents the equilibria and stable phases at 90°. It is the same equilateral triangle of unit height used in the previous paper by McBain and Burnett, in which the respective corners represent 1 mol. of pure anhydrous sodium palmitate, 1 mol. of sodium chloride, and 1 kilo. of water; and in which the co-ordinates

are the fractions of these three quantities the sum of which for each point on the diagram is unity. Although this is not so easily read as the rectangular diagram given below, it is much more satisfactory for a complete survey of the field. ·

Nearly half the diagram is occupied by the field of isotropic solutions beginning with pure water and remaining single homogeneous liquids when soap and salt are added up to rather high concentrations. The internal equilibria of these solutions, which range from crystalloidal to wholly colloidal, are discussed in other communications. (It may be mentioned, however, that "middle soap," like isotropic soap, is a colloidal electrolyte.) The isotropic field extends up to saturated aqueous solutions of sodium chloride.

There are three other fields representing single phases of varying composition; namely, curd fibres (at the top of the diagram), anisotropic "neat soap," and anisotropic "middle soap." There is but one phase of constant composition, namely, crystalline sodium chloride, which is found at the lower right hand point of the diagram.

There are seven fields in which two phases each of varying composition co-exist; namely, (A) "middle soap" and isotropic solution, (B) "middle soap" and "neat soap," (C) "neat soap" and curd fibres, (D) "neat soap" and isotropic solution (which latter in this region is called "nigre" by soap boilers), (E) "neat soap" and isotropic solution (which is always called "lye"), at the bottom of the diagram, (F) a small region in which the isotropic solution separates into two layers corresponding approximately to nigre and lye, and (G) curd fibres and lye up to its saturation point with salt. Whenever three phases co-exist at barometric pressure, each is of fixed composition, as shown by the diagram. Solid sodium chloride cannot exist in contact with any phase except saturated lye and curd fibres.

The chief fields occurring during soap-boiling processes are (D) (during fitting), (E) (when rather more salt has been added but not enough to salt or grain out); but it is only when the neat soap is cooling in the frames that (C) is met with through the separation of curd fibres, at much lower temperatures.

The forms of the fields for neat soap and for curd fibres are only approximately known, but the general position is fixed by an accurate knowledge of one or two points in each.

Fig. 2 is similar to Fig. 1, but is very much more easily read, since rectangular co-ordinates are used. For convenience of comparison with soap-boiling data, technical units are employed.* The diagram

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* This possibility of direct comparison is specially important, since in ordinary soap boiling glycerol also is present and it is seldom that a complete analysis of each phase is available.

refers to 100°. It will be observed that the tie lines are straight; in other words, as on the triangular diagram, any point in a heterogeneous field quantitatively represents the respective amounts of the two phases lying at the ends of the straight tie line passing through that point.

Fig. 3 represents the effect of cooling solutions to a lower temperature, such as 68°, at which the curd fibre of sodium palmitate is so much less soluble that no soap solutions concentrated enough

FIG. 2.
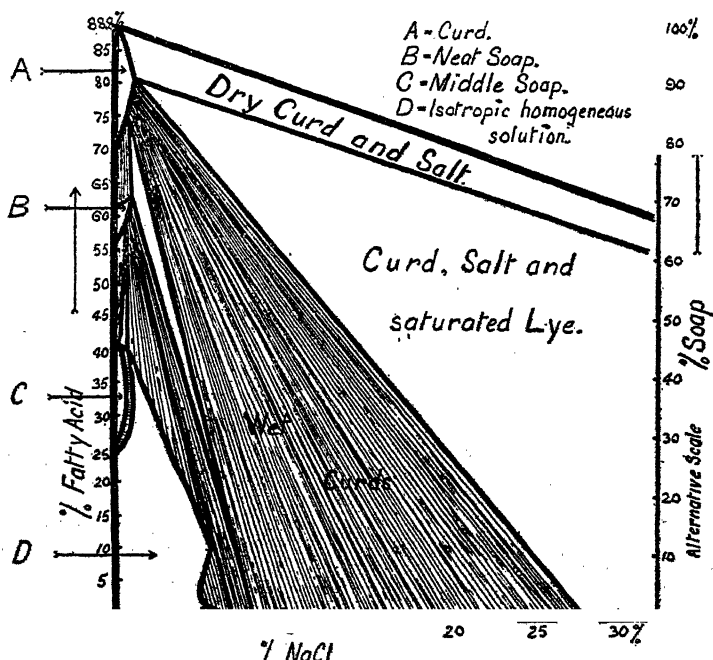
Phase rule diagram at 100°, *concentrations being expressed in grams of fatty anhydride and grams of salt per* 100 *grams of total system. The areas correspond to those in Fig.* 1.

to form " middle soap " or " neat soap " can exist and even half the isotropic field has been destroyed. At a temperature only about 10° lower, the solubility of sodium palmitate is reduced to an extremely narrow field of lye—along the bottom of the diagram, with curd fibres at the top, all in between being wet curds with enmeshed lye. At room temperature, sodium palmitate is practically insoluble and the only systems met with are wet and dry curds. The diagram shows two (approximate) solubility curves for 72° and 76°, respectively, and there are also dotted in the boundary

lines of the liquid phases at 80°, at which temperature the solubility of sodium palmitate is so much greater that neat soap is the only form of liquid concentrated enough to be capable of crystallising.

Figs. 4 and 5 present the data for the accurate mapping of the limits of the field of isotropic solutions at temperatures ranging from 60° to 150°. The solutions at 60° are of course under-cooled with respect to separation of curd fibres.

FIG. 3.
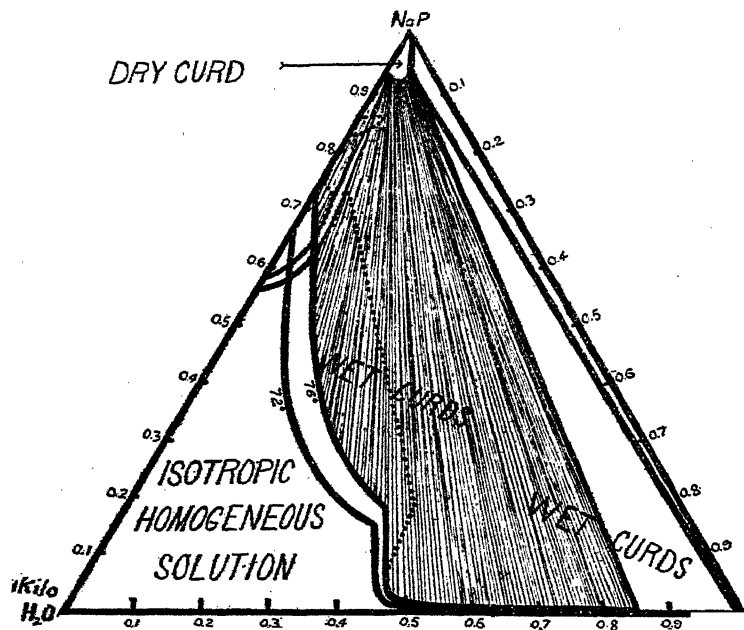
Maximum concentrations of solutions which can exist at 76° (and at 72°) when not supersaturated with curd fibres. The fields enclosed by the dotted lines within the shaded areas are soap solutions which have been destroyed by the curd fibres crystallising out at 76°.

The diagram at 150° is particularly interesting because it shows the concentrations of solutions of pure soap in the absence of salt at which isotropic solutions, " middle soap " and " neat soap " exist. Up to $2\cdot3N_w$ at 150°, solutions of sodium palmitate are isotropic. Solutions slightly more concentrated cannot be made owing to the separations of " middle soap." " Middle soap " exists between the concentrations $2\cdot5N_w$ and $3\cdot0N_w$ and this is nearly the maximum temperature at which " middle soap " can exist at all. It is remarkable that in still higher concentrations isotropic solutions are again formed and the diagrams show clearly

how these concentrated isotropic solutions continuously pass through the solutions containing salt to the dilute isotropic solutions. At still higher concentrations of aqueous sodium palmitate, the further anisotropic phase, "neat soap," is formed.

Outline of Previous Work.*

Chevreul's view that a bar of soap consists of definite hydrates has been maintained even by Lewkowitsch, who speaks of "water of constitution." Merklen attacked this, assuming that such soap

FIG. 4.
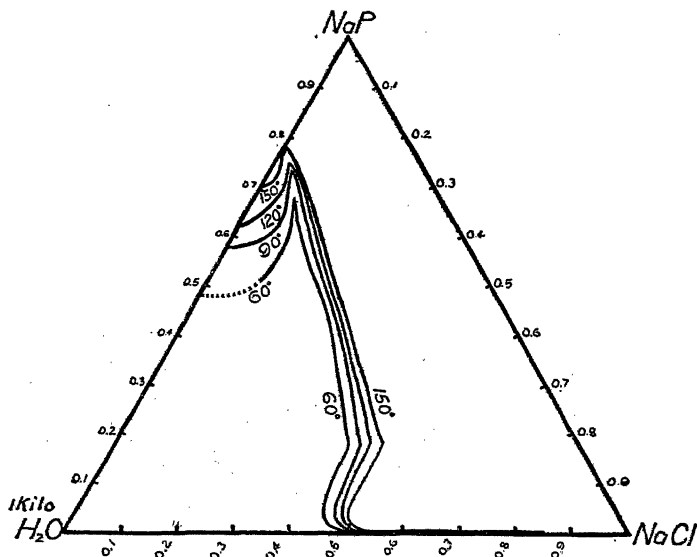
Solubility curves of salt and sodium palmitate at 60°, 90°, 120° and 150° showing the extreme limits of the field of homogeneous isotropic solutions capable of existing at these temperatures.

is a "sorption compound." Since such a bar, whether of household soap or toilet base, is obtained merely by the cooling of neat soap removed from the soap pan, we see, however, that, although its total composition is necessarily that of the original sample of "neat soap," its constitution and structure have nothing to do with those of "neat soap." Actually it is a heterogeneous mixture, consisting of innumerable hydrated curd fibres enmeshing one or more solutions containing the more soluble soaps. The bar of soap is thus a heterogeneous mixture necessarily of the same total

* See Fourth Colloid Report of the British Association for the Advancement of Science, 1922, 249.

composition as the "neat soap" which was taken from the soap pan.

Merklen's monograph in 1907 constituted a great advance in the scientific treatment of this subject in that it was the first attempt to apply the phase rule to the soap-boiling processes. Merklen worked with commercial soaps and oils and recognised two of

FIG. 5.
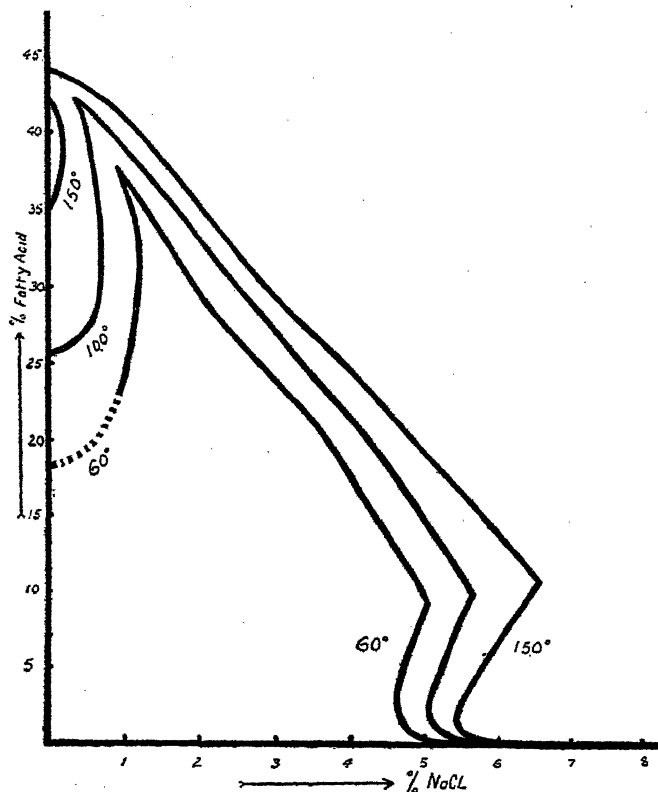
Limits of existence in technical units of homogeneous isotropic solutions con-taining salt and soap at 60°, 100°, and 150° showing the two regions in which solutions of pure soap form isotropic solutions at 150°.

the systems here described, namely, "neat soap" with "nigre" and "lye," respectively. It appears, however, that his soap-boiling technique was faulty in that he did not secure proper separation.

Richert (*Diss.*, Karlsruhe, 1911), working with dilute solutions of pure soaps, discovered the two-layer system "nigre-lye." He was the first to show that various salts have a similar effect so that

by the use of numerical factors it is possible to predict the amounts of each which will replace the others.

Further, it is evident from scattered information, published and unpublished, there is little or no fractionation when mixtures of soaps separate into liquid layers. Hence it is evident that as far as formation of liquid layers is concerned the most complicated mixture of commercial oils and fats containing a number of electrolytes such as hydroxide, carbonate, chloride, sulphate, etc., exhibits a behaviour similar to that of a three-component system such as is described in the present paper. It is only when sufficient salt has been added to cause a separation of some of the least soluble soaps as curd fibres that fractionation of the soaps sets in and the behaviour is that of a more complicated system. Fortunately, as has been seen, this occurs only to a minor extent in the soap pan, since graining out is never carried to completion.

Bätz (*Diss.*, Karlsruhe, 1918) and M. Thörl (*Diss.*, Karlsruhe, 1918) worked with commercial oils, studying neat soap together with lye or nigre or both. They considered that the three layers simultaneously present were not of fixed composition, but we can attribute this to a form of experiment in which equilibrium was not perfectly attained. Their results, like those for other published data on analysis of commercial products, agree essentially with the triangular diagram explained in this paper; but, not knowing of the existence of " middle soap," they regarded " neat soap " and " nigre " as continuous with each other instead of being wholly separate phases. The present paper and the previous one with Burnett show that the total number of possible two-layer systems is seven. The present paper has been written with a knowledge of further comprehensive experiments carried out in this laboratory by A. V. Pitter and W. J. Elford, and others.

One single example may be given to illustrate the usefulness of the phase rule diagrams developed in our present paper. Bergell (*Seifens. Ztg.*, 1924, **51**, 591) has published technical experiments on a commercial scale which seemed to show that in passing from a very close fit to a very open fit the amount of salt in the neat soap passed through a minimum. For a very close fit or for a very open fit the quantity of salt in the upper layer was 1%, whereas for a fit intermediate between that customary for soap base and bar soap only 0·3% of salt was present. It is obvious from purely geometrical considerations that it is impossible to place such a curve as that found by Bergell upon the diagrams given in the present paper or upon any of the numerous diagrams of similar types for commercial soaps without cutting across the lines or, in other words, without entering the heterogeneous region of the two-layer system, neat

H H 2

soap-nigre. It follows with certainty that the result obtained by Bergell was due to faulty or incomplete separation of nigre and neat soap in the closer fits.

Summary.

1. For the first time a complete survey has been made of the stable systems of water, soap and salt.

2. The following phases can exist in any soap system, whether prepared from a commercial oil or from pure soap; true lamellar crystals; crystalline curd fibres; anisotropic liquid "neat soap"; anisotropic liquid "middle soap" (existence previously unsuspected); isotropic liquid. All the soap-boiling operations depend on equilibria between these phases.

3. The limits of the field of existence of isotropic liquid solutions of sodium palmitate with and without salt have been accurately determined for temperatures up to 150°. This single phase includes wholly crystalloidal and wholly colloidal solutions and ranges at sufficiently high temperatures from pure water up to pure anhydrous liquid sodium palmitate, the two being miscible in all proportions above 316°.

4. As a first and close approximation the contents of a soap pan, although prepared from commercial oils and fats each containing many constituents, and although containing many electrolytes, behaves like a simple three-component system apart from crystallisation.

CXXI.—*The Nature of the Alternating Effect in Carbon Chains. Part II. The Directing Influence of the α-Methoxyvinyl Group in Aromatic Substitution.*

By CHRISTOPHER KELK INGOLD and EDITH HILDA INGOLD.

As explained in Part I (this vol., p. 513), these investigations have been undertaken in order to obtain insight into the nature of the alternating effect, the existence of which is implied both in the hypothesis of alternating affinity-demand and in the hypothesis of induced polarities.

For the present, attention is being confined to directive influence in aromatic substitution, and in Part I it was shown that the

nitroso-group falls within the *op*-directing series. The nitroso-group is one of the very few groups as to the directive effect of which the theories of alternating affinity and induced polarity appear to differ in their predictions; and the observed facts agree with the idea of alternating affinity rather than with that of induced polarity, unless, indeed, in the latter case, such flexibility of procedure be admitted as would completely destroy the prophetic power of this theory in all potential test-cases.

Since the above facts were communicated, three arguments have been advanced in the cause of the polarity theory :

(i) That since in the nitroso-group there are two competing negative key-atoms, the case is too complicated for satisfactory prediction (Lapworth, *Chem. and Ind.*, 1924, **43**, 1294).

(ii) That oxygen, although "usually" more negative (or negatively active) than nitrogen, suffers handicap in the nitroso-group owing to the greater distance of the oxygen atom from the benzene ring (*idem, ibid.*).

(iii) That a different mechanism may (should ?) be assumed when the atom directly attached to the benzene ring contains a " lone-pair " of electrons (Robinson, *ibid.*, p. 1297).

There are logical answers to all these objections,* but it is perhaps of greater importance that they are amenable to experimental treatment; and experiments are now described which were devised as a test of their validity.

A substituent group was selected to fulfil the following conditions :

(*a*) That opposite forecasts as to its directive effect shall flow from the simple application of the principles of alternating affinity and induced polarity (*vide* Part I, *loc. cit.*).

(*b*) [*Condition to obviate objections* (i) *and* (ii).] That either the group shall contain only one negative key-atom, or, if there be several, these shall be harmoniously situated.

(*c*) [*Condition to obviate objection* (iii).] That the atom by which the group is attached to the benzene ring shall not contain a " lone-pair " of electrons.

It may be stated at once that even when these conditions are fulfilled orienting effects are observed which still agree with the idea of alternating affinity, and still run counter to that of induced polarity.

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* Arguments (i) and (ii) apply equally to the nitro- and ammonium-salt groups ($-NO_2$ and $-NH_3X$), which happen to behave satisfactorily from the polarity point of view. Thus, in advancing these two arguments, a great part of the case for the polar conception of orienting action is given away. The logical reply to (iii) has been made by Flürscheim (*Chem. and Ind.*, 1925, **44**, 33, 34).

Condition (c) was secured by making the connecting atom a carbon atom, condition (b) by attaching to it only one oxygen atom (and, of course, no nitrogen atom), and condition (a) by introducing a double bond, the residual affinity from which determines the effect to be expected from the theory of alternating affinity (compare Flürscheim, *J. pr. Chem.*, 1902, **66**, 321). The combined result of these structural requirements is represented in the α-methoxyvinyl group, the predicted orienting effects of which are expressed in the following formulæ :
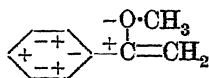
(Alternate polarities :
m-directive action.)
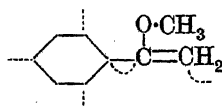
(Alternating affinity :
op-directive action.)

The directing influence of the α-methoxyvinyl group in nitration is practically exclusively ortho-para; that is to say, it is in agreement with the hypothesis of alternating quantity of affinity.

It should be added that certain results are capable of interpretation on the basis that a nitro-group first enters the ω-position, giving (I), which then, on further nitration, yields (II) and (III) :

$$\text{(I.)} \quad C_6H_5 \cdot C(OMe) : CH \cdot NO_2 \longrightarrow \begin{cases} (o)NO_2 \cdot C_6H_4 \cdot C(OMe) : CH \cdot NO_2 \text{ (II.)} \\ (p)NO_2 \cdot C_6H_4 \cdot C(OMe) : CH \cdot NO_2 \text{ (III.)} \end{cases}$$
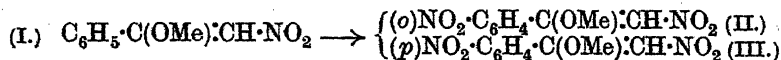
If this were so, the real directing group to which the products (II) and (III) owe their formation would not be $-C(OMe):CH_2$, as intended, but $-C(OMe):CH \cdot NO_2$. This, however, would not explain the lack of agreement with the application of alternate polarities, because on attaching to the atoms of the nitro-group those plus and minus signs which best explain its general behaviour from the polarity standpoint, it is at once seen that this group, far from competing with, would actually reinforce, the key-negative influence of the ethereal oxygen.

Conclusion.—The inference recorded in Part I appears to be confirmed by these experiments.

EXPERIMENTAL.

α-Methoxystyrene was prepared from ethyl phenylpropiolate by a series of reactions analogous to those investigated by Moureu (*Compt. rend.*, 1904, **137**, 260; *Bull. Soc. chim.*, 1904, **31**, 498, 525; see also Claisen, *Ber.*, 1898, **31**, 1020).

Ethyl phenylpropiolate (50 g.) was heated for 2 hours on the water-bath with 140 c.c. of methyl-alcoholic sodium methoxide prepared from 6·9 g. of sodium. The oil, b. p. 140—147°/10—

11 mm., extracted with ether after pouring into ice-water consisted principally of a mixture of methyl and ethyl ββ-dimethoxy-β-phenyl-propionates, containing, however, traces of the β-methoxycinna-mates. Without purification, the oil was converted into a mixture of methyl and ethyl methoxycinnamates by heating in an oil-bath at 200° for 1 hour, when methyl alcohol was evolved. The mixed esters, b. p. 144—149°/8 mm., were then hydrolysed by hot aqueous-alcoholic potassium hydroxide, exactly as described by Moureu in the case of methyl methoxycinnamate, and the free acid, after due purification, was converted by heat and subsequent distillation into α-methoxystyrene.

Nitration of α-Methoxystyrene.—The methoxystyrene (5 g.) was allowed to flow through a capillary tube during about 30 hours into 22·5 g. of pure nitric acid kept at − 20° and well shaken. The product was isolated by pouring on to ice and extracting with ether. Washing with aqueous sodium carbonate removed a small quantity of a yellow, crystalline, acidic substance, which has not yet been investigated, and the residual ether solution yielded a yellow oil, which could be distilled without decomposition only at about 1 mm. Three principal fractions were obtained, (*a*) an almost colourless, mobile oil, b. p. below 60°, (*b*) a fairly mobile, yellow oil, b. p. 88—95°, (*c*) a rather viscous, yellow oil, b. p. 128—132° (chief fraction).

Fraction (*a*) contained qualitative traces of nitrogen, but consisted chiefly of acetophenone, the normal hydrolysis product of α-methoxystyrene.

Fraction (*b*) was a mixture consisting apparently of the mono-nitration products of α-methoxystyrene and acetophenone. The quantity was too small to permit of a detailed investigation, but on oxidation with potassium permanganate benzoic acid and the three nitrobenzoic acids were obtained.

Fraction (*c*) contained the dinitration products. On redistillation, it gave no indication of separating into fractions, almost the whole passing over at 128—130°/1 mm. The figures obtained on analysis (Found : C = 48·5; H = 3·6. $C_9H_8O_5N_2$ requires C = 48·2; H = 3·6%) corresponded with those required for a dinitromethoxy-styrene, but all attempts to crystallise it proved fruitless. It was observed, however, that all the α-alkyloxystyrenes described in the literature are liquids, even those of fairly high molecular weight like α-phenoxy- and the three α-tolyloxy-styrenes, and it was therefore decided to determine the constitution of the oil by oxidation. The results of these experiments show that it consists to the extent of about 65% of ωp-dinitro-α-methoxystyrene, the remainder being the isomeric ωo-compound.

Oxidation of ωo-*Dinitro-α-methoxystyrene and* ωp-*Dinitro-α-methoxystyrene* (II *and* III).—The mixture of these isomerides (2·5 g.) was thoroughly emulsified with a little water and then vigorously shaken in the cold with successive small quantities of a solution of 20 g. each of potassium permanganate and sodium hydrogen carbonate in 1 litre of water, the additions being timed to keep pace with decoloration. When 50 c.c. had been added, the mixture was transferred to the steam-bath, and the addition of permanganate solution continued. No great diminution in the velocity of the reaction was noticed when 200 c.c., the theoretical amount for the formation of $NO_2 \cdot C_6H_4 \cdot CO_2Me + CO_2 + HNO_3$, had been added, and the process was therefore continued until 370 c.c. had been used, and the product was relatively stable to permanganate. The small excess of the reagent was removed with hydrogen peroxide, and the solution filtered. The precipitate was thrice suspended in water and treated with steam, and the combined filtrates were extracted with ether, evaporated to small bulk, and acidified. The small oily residue obtained on evaporating the ethereal extract was boiled for 16 hours with 20% hydrochloric acid, and the resulting solution made alkaline, extracted with ether, and reacidified. After combining the two acid solutions, the organic acids were isolated by extraction with ether.

The residue from the ether was distilled in steam for a short time, and the absence of benzoic acid proved by examining the first portions of the distillate. It was then crystallised from much boiling water, from which, on cooling, nearly pure *p*-nitrobenzoic acid separated, m. p. 230—234°. This was finally purified by crystallisation from glacial acetic acid, and identified by its m. p. (237—238°), by analysis (Found : C = 50·6; H = 3·2. Calc., C = 50·3; H = 3·0%), by direct comparison and mixed m. p. with a genuine specimen, and by conversion into its methyl ester (m. p. 96°), which was similarly compared.

The mother-liquors contained a much more soluble acid, m. p. about 140—143°, which, from mixed m. p. determinations with *o*-nitrobenzoic acid (m. p. 146—147°) and *m*-nitrobenzoic acid (m. p. 140—141°), appeared to consist mainly of *o*-nitrobenzoic acid. In order to detect any *m*-nitrobenzoic acid, if present, the specimen was treated successively with phosphorus pentachloride and methyl alcohol, the methyl esters being isolated by extraction with pure ether after addition of water. Since methyl *m*-nitrobenzoate is crystalline and sparingly soluble in cold methyl alcohol, whilst methyl *o*-nitrobenzoate is a liquid completely miscible with that solvent, any *m*-ester present should have separated when methyl alcohol was added to the mixed esters and seeded with a

crystal of the *m*-ester; for experiments with artificial mixtures of the two isomerides indicated this method to be an efficient one for the detection and separation of small quantities of the *m*-compound. In the case under description, however, no separation of *m*-ester occurred, although a very small quantity of methyl *p*-nitrobenzoate crystallised. The liquid ester was therefore rehydrolysed with hydrochloric acid, and the *o*-nitrobenzoic acid so obtained crystallised from dilute acetic acid and identified by its m. p. (146—147°), analysis (Found : C = 50·5; H = 3·2. Calc., C = 50·3; H = 3·0%), and comparison with an authentic specimen.

Treatment of Fraction (*b*).—The oxidation of this fraction by permanganate was carried out as in the preceding experiment, and the various acids so produced were separated in a similar way. Benzoic acid was isolated by distillation in steam, *p*-nitrobenzoic acid by crystallisation from water, whilst the more soluble but less volatile *o*- and *m*-acids were separated through their methyl esters as described above (for methyl *m*-nitrobenzoate, m. p. 79°, found : C = 53·1; H = 4·1. Calc., C = 53·0; H = 3·9%).

Treatment of Fraction (*a*).—On redistillation, this yielded a colourless oil, b. p. 88—92°/12 mm., which was identified as acetophenone by means of its semicarbazone. The latter was prepared using semicarbazide acetate and crystallised from ethyl alcohol, from which needles separated, m. p. 200°, which did not depress the m. p. of a genuine specimen of acetophenonesemicarbazone.

CXXII.—*Bromo-derivatives of* m-*Hydroxybenzaldehyde.*

By HERBERT HENRY HODGSON and HERBERT GREENSMITH BEARD.

ALTHOUGH the 6-bromo-derivative (Pschorr, *Annalen*, 1912, **391**, 23) and the 2 : 4 : 6-tribromo-derivative (Krause, *Ber.*, 1899, **32**, 122) have been described, little attention has hitherto been directed to the bromination of *m*-hydroxybenzaldehyde.

Tribromination of the aldehyde in aqueous solution at 50° is sufficiently quantitative to be suitable for its estimation, and regulated bromination to the 6-mono-, 4 : 6-di-, and 2 : 4 : 6-tribromo-derivatives can be carried out in chloroform or carbon tetrachloride; Rosenmund, Kuhnhenn, and Lesch's method of moderated bromination in presence of a quinoline salt (*Ber.*, 1923, **56**, 2042) does not give better results.

H H*

2-, 4-, and 6-Bromo-3-hydroxybenzaldehydes were prepared synthetically from *m*-hydroxybenzaldehyde *via* the corresponding nitro-compounds. In the nitration, good yields of 6- and 4-nitro-3-hydroxybenzaldehydes were obtained, but to isolate the 2-nitro-compound superheated steam was required and its use was attended with considerable destruction of material. The silver salts of these nitro-compounds have characteristic colours and differ in stability towards boiling water. Only poor yields of 6-bromo-3-hydroxybenzaldehyde were obtained from the 6-nitro-compound, and these are attributed to secondary changes occurring during the reduction stage—the amino-compound is readily oxidised and is converted by hydrochloric acid into a red amorphous substance corresponding with the formula $HO\cdot C_6H_3{<}^{\text{C}H}_{\text{N}}$ (it is noteworthy that Friedländer prepared 6-chloro-3-hydroxybenzaldehyde from the nitrocresol, not from 6-nitro-3-hydroxybenzaldehyde).

An attempt to introduce bromine into the *p*-nitrophenylhydrazone of 4-amino-3-hydroxybenzaldehyde by the Sandmeyer reaction led to the ready production of *p*-nitrophenylazoimide, and therefore to work (now in progress) on the decomposition of hydrazones.

The colours of the *p*-nitrophenylhydrazones of the various hydroxy-aldehydes are for the most part in agreement with Chattaway and Clemo's generalisation (J., 1923, **123**, 3041); their methyl ethers are yellower in shade and have the same colour in alkaline solution. In general the m. p.'s of the ethers are lower than those of the hydroxy-aldehydes.

EXPERIMENTAL.

Direct Bromination of m-*Hydroxybenzaldehyde.*—In aqueous solution it was impossible to regulate the bromination, and rapid addition of excess of bromine in the cold gave an incompletely tribrominated product (Found : Br, 62·6. Calc., Br, 66·8%). Careful addition at 50°, however, gave pure 2 : 4 : 6-tribromo-3-hydroxybenzaldehyde of m. p. 119° (Krause), although rapid addition still produced mixtures. Brominated at 50° by the standard bromide-bromate method with very cautious acidification, 0·2421 g. of *m*-hydroxybenzaldehyde absorbed 0·4684 g. of bromine (equiv. to 2·9 atoms).

Regulated bromination in chloroform. A solution of *m*-hydroxybenzaldehyde (10 g. in 100 c.c. of chloroform) was treated with the calculated quantity (for monobromination) of bromine in 30 c.c. of chloroform. The crude product (15 g.), after extraction with 50 c.c. of 6% sodium carbonate solution and crystallisation from dilute acetic acid, gave 6-bromo-3-hydroxybenzaldehyde,

m. p. 134° (compare Pschorr, *loc. cit.*). A blackish-green by-product containing bromine was insoluble in dilute acetic acid but dissolved in aqueous sodium hydroxide. On acidification of the sodium carbonate extract (above) a mixture of 6- and 4-bromo-3-hydroxybenzaldehydes was precipitated; these were converted into the p-nitrophenylhydrazones, which were separated by fractional crystallisation from chloroform, that of the 6-bromo-compound being the less soluble.

With the quantities of bromine and solvent given above, the 6- and the 4-bromo-compound were each converted into 4 : 6-di-bromo-3-hydroxybenzaldehyde, m. p. 139°. The temperature was slowly raised to 50°, when hydrogen bromide was evolved. The mixture was heated under reflux for 1 hour, and the crude product, m. p. 138°, recrystallised from dilute acetic acid. There were no by-products (Found : Br, 57·4. Calc., Br, 57·2%).

2 : 4 : 6-Tribromo-3-hydroxybenzaldehyde, m. p. 119°, was obtained in like manner.

Regulated bromination in carbon tetrachloride. The crude mono-bromo-compound melted at 132—133° and no by-product was formed (Found : Br, 40·4. Calc., Br, 39·8%). Since, however, 5 g. of m-hydroxybenzaldehyde dissolve in 200 c.c. of carbon tetrachloride and in 75 c.c. of chloroform, the use of the latter solvent is preferable in bulk preparations.

The crude product obtained by the method of Rosenmund, Kuhnhenn, and Lesch (*loc. cit.*) melted at 128—130°.

Preparation of the Mononitro-3-hydroxybenzaldehydes.—Pschorr's method of nitration (*loc. cit.*; see also Friedländer, *Ber.*, 1914, **47**, 3040) was modified only in that a solution of twice the concentration was used. The yield of precipitated nitro-compounds was 117 g. from 100 g. of m-hydroxybenzaldehyde; 8 g. more were salted out from the mother-liquor. From the total product, 48 g., 32 g., and 5 g. of 6-, 4-, and 2-nitro-3-hydroxybenzaldehyde, respectively, were obtained.

The *silver* salts of 6-, 4-, and 2-nitro-3-hydroxybenzaldehyde form light brownish-yellow leaves (Found : Ag, 38·9), brick-red plates (Found : Ag, 39·1), and dark red needles (Found : Ag, 38·94. Calc., Ag, 39·4%), respectively. The first is soluble in hot water, but decomposes rapidly in a boiling solution. The second is almost insoluble in cold water and is stable in a hot solution. The third is soluble in cold water and is less stable than the first.

Preparation of the Bromo-3-hydroxybenzaldehydes.—The preceding nitro-compounds were reduced by the following method. A suspension of 5 g. in 50 c.c. of water was treated gradually with 20 g. of solid sodium hyposulphite, and the mixture was heated on the

water-bath for 15 minutes, cooled, carefully acidified with hydro-
bromic acid, and treated as in the Sandmeyer reaction; the product
was extracted with ether.

From 6-nitro-3-hydroxybenzaldehyde, 6-bromo-3-hydroxybenz-
aldehyde was obtained in but poor yield. After crystallisation
from dilute acetic acid, it melted at 133—134°, alone or mixed
with the corresponding bromo-compound obtained from *m*-hydroxy-
benzaldehyde. Attempts to improve the yield by reducing with
ferrous sulphate and ammonia, or by reduction of various deriv-
atives of 6-nitro-3-hydroxybenzaldehyde (acyl derivatives, oxime,
acylated oxime, etc.) were unsuccessful.

In the preparation of 4-*bromo-3-hydroxybenzaldehyde* from the
nitro-compound it was found advantageous, after the reduction,
to diazotise the product in hydrochloric acid, add sodium acetate,
and then follow the usual Sandmeyer procedure. The 4-bromo-
compound, m. p. 131·5°, is only slowly volatile in steam and is
partly decomposed thereby (Found : Br, 39·2. $C_7H_5O_2Br$ requires
Br, 39·8%).

2-*Bromo-3-hydroxybenzaldehyde* melts at 141—142° (Found : Br,
39·5%).

p - *Nitrophenylazoimide.* — 4 - Amino - 3 - hydroxybenzaldehyde -*p* -
nitrophenylhydrazone was diazotised in hydrochloric acid, and the
product decomposed on the water-bath with cuprous chloride.
Distillation with steam removed *p*-nitrophenylazoimide, which
melted at 69·5° after crystallisation from alcohol (Found : N, 34·7.
Calc., N, 34·1%).

Preparation of 6-, 4-, and 2-Bromo-3-methoxybenzaldehydes.—The
corresponding hydroxy-aldehyde (1 mol.), dissolved in boiling
10% sodium hydroxide solution (2 mols.), was treated with methyl
sulphate (1·3 mols.). After 1 hour, the mixture was distilled with
steam, and the methoxy-compound, which separated from the
distillate on cooling, recrystallised from dilute alcohol. 6-Bromo-
3-methoxybenzaldehyde melts at 76° (Pschorr gives m. p. 76°),
the 4- and the 2-bromo-compound at 74° and 45—46°, respectively.

These compounds were also prepared from the corresponding
nitromethoxybenzaldehydes. The nitro-compound (10 g.), dis-
solved in boiling alcohol (50 c.c.), was treated with sodium disulphide
(14 g. of cryst. sodium sulphide, 3·5 g. of sulphur, 15 c.c. of water).
After boiling for 3 hours, the solution was diluted, and extracted
with ether. The residue after evaporation of the ether was dissolved
in 10 c.c. of alcohol, and 10 g. of sulphuric acid (50%) were added,*

* If the acid is added to the free amine obtained from the ether extract,
a hard, insoluble, red substance is produced (compare Khotinsky, *Ber.*, 1909,
42, 3097).

when the finely-divided sulphate of the amine was obtained. (The sulphate of 4-amino-3-methoxybenzaldehyde has a brilliant red colour which fades on keeping; the sulphate of 4-amino-3-hydroxybenzaldehyde behaves similarly.) The sulphate was diazotised, and the product treated with cuprous bromide.

6-Bromo-3-methoxybenzaldehyde was thus obtained from the 6-nitro-compound in good yield (in sharp contrast to the trace of 6-bromo-3-hydroxybenzaldehyde obtained from 6-nitro-3-hydroxybenzaldehyde). The yield of the 4-bromo-compound (Found : Br, 37·0%) was 4 g. from 10 g. of 4-nitro-3-methoxybenzaldehyde. The 2-bromo-compound formed fine white needles (Found : Br, 37·2%). All three products were contaminated with oily impurities which were probably substances of the anthranil type.

4 : 6-*Dibromo-3-methoxybenzaldehyde*, obtained by methylation of the hydroxy-compound in aqueous sodium hydroxide, melted at 110° after crystallisation from dilute alcohol (Found : Br, 53·8. $C_8H_6O_2Br_2$ requires Br, 54·4%).

Oximes of the Nitro- and Bromo-hydroxybenzaldehydes and of the Bromomethoxybenzaldehydes.

General Method of Preparation.—An alcoholic solution of the aldehyde (1 mol.) was treated with aqueous hydroxylamine hydrochloride (1 mol.) and sodium acetate, the mixture boiled for 1 hour, and the oxime allowed to crystallise from the cooling and slowly evaporating solution.

6-*Nitro-3-hydroxybenzaldoxime :* Pale yellow needles by addition of light petroleum to an ethereal solution; m. p. 178—179° (the m. p. of the oxime crystallised from water is never higher than 172°) (Found : N, 15·35. $C_7H_6O_4N_2$ requires N, 15·4%). Yellow sodium salt.

4-*Nitro-3-hydroxybenzaldoxime :* Deep yellow needles, m. p. 164° (Found : N, 15·6%). Brilliant red sodium salt, sparingly soluble in water.

2-*Nitro-3-hydroxybenzaldoxime :* Needles paler than the preceding; m. p. 172·5° (Found : N, 15·6%). Much more difficult to prepare than either of the preceding oximes. Sodium salt not so vividly red as that of the 4-nitro-compound.

6-*Bromo-3-hydroxybenzaldoxime :* White needles from water; m. p. 157° (Found : Br, 36·5. $C_7H_6O_2NBr$ requires Br, 37·0%). Pale yellow sodium salt.

4-*Bromo-3-hydroxybenzaldoxime :* White, microcrystalline powder from water; m. p. 173—174° (Found : Br, 36·6%).

2-*Bromo-3-hydroxybenzaldoxime :* Fine, white needles from water; m. p. 148° (Found : Br, 36·7%).

4 : 6-*Dibromo-3-hydroxybenzaldoxime :* m. p. 243° (Found : Br, 54·0. $C_7H_5O_2NBr_2$ requires Br, 54·2%).

6-*Bromo-3-methoxybenzaldoxime :* Silky, white needles from dilute alcohol; m. p. 117° (Found : Br, 34·8. $C_8H_8O_2NBr$ requires Br, 34·75%).

4-*Bromo-3-methoxybenzaldoxime :* White needles, m. p. 94·5° (Found : Br, 34·9%).

2-*Bromo-3-methoxybenzaldoxime :* White needles, m. p. 148° (Found : Br, 34·2%).

Carboxylic Acids from the Bromomethoxybenzaldehydes.

General Preparation.—The aldehyde (1 mol.) was heated for 2 hours on the water-bath with a solution of potassium permanganate (0·66 mol.) and sodium carbonate. The solution was treated with sodium bisulphite, acidified with hydrochloric acid, and the product recrystallised from water.

6-Bromo-3-methoxybenzoic acid : White needles, m. p. 162° (Pschorr gives m. p. 162°).

4-*Bromo-3-methoxybenzoic acid :* White needles, m. p. 219—220° (Found : Br, 34·5. $C_8H_7O_3Br$ requires Br, 34·6%).

2-Bromo-3-methoxybenzoic acid : White needles, m. p. 157—158° (Pschorr gives m. p. 153—155°. His product probably contained the 4-bromo-acid as impurity) (Found : Br, 34·4%).

4 : 6-Dibromo-3-methoxybenzoic acid : Stout, white needles from dilute alcohol; m. p. 202—203° (Bauer and Vogel, *J. pr. Chem.*, 1913, **88**, 329, give m. p. 201—202°).

The p-*Nitrophenylhydrazones.*

General Preparation.—The aldehyde, dissolved in rather dilute acetic acid, was treated gradually with an aqueous solution of *p*-nitrophenylhydrazine until precipitation ceased. The hydrazone was formed in quantitative yield. The method is generally applicable to the estimation of aldehydes. A hydrazone precipitated from aqueous solution is paler in colour than the same hydrazone crystallised from alcohol, chloroform, or acetone. The hydroxy-hydrazones all exhibit a colour change when heated, becoming paler at 150—160°; the colour returns just prior to fusion, when decomposition occurs. The methoxy-hydrazones behave normally and are stable when heated. (The colour produced by addition of alcoholic potassium hydroxide to an alcoholic solution of the hydrazone is given immediately after the m. p.)

6 - *Nitro* - 3 - *hydroxybenzaldehyde* - p - *nitrophenylhydrazone :* Deep orange-red needles; decomp. 250°, m. p. above 300°. Reddish-violet (Found : N, 18·9. $C_{13}H_{10}O_5N_4$ requires N, 18·5%).

4-*Nitro*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Redder orange than the preceding; m. p. 265—266°. Bluish-violet.

2-*Nitro*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Brick-red needles, m. p. 240—250° (decomp.). Reddish-violet (Found : N, 19·0%).

4-*Nitro*-3-*methoxybenzaldehyde*-p-*nitrophenylhydrazone :* Brick-red needles, m. p. 236—238°. Violet-blue, very different from the other colours and in accord with Chattaway's observation (*loc. cit.*) with regard to two nitro-groups in para positions (Found : N, 17·8. $C_{14}H_{12}O_5N_4$ requires N, 17·7%).

There was no change in colour on heating any of the above alcoholic solutions.

6-*Bromo*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Reddish-orange needles, m. p. 240—243°. Deep claret (Found : Br, 23·9. $C_{13}H_{10}O_3N_3Br$ requires Br, 23·8%).

The 4-*bromo*-isomeride : Brick-red needles, m. p. 210—212°. Decomp. above 220°. Deep claret (Found : Br, 23·7%).

The 2-*bromo*-isomeride : Red needles, m. p. 241°. Deep claret (Found : Br, 23·2%).

The claret shade is deepest for the 4-bromo- and lightest for the 6-bromo-compound.

6-*Bromo*-3-*methoxybenzaldehyde*-p-*nitrophenylhydrazone :* Orange needles, m. p. 225°. No decomp. Deep claret (Found : Br, 22·3. $C_{14}H_{12}O_3N_3Br$ requires Br, 22·8%).

The 4-*bromo*-isomeride : Orange needles, m. p. 246°. No decomp. Deep claret (Found : Br, 22·3%).

The 2-*bromo*-isomeride : Yellow needles, m. p. 206—208°. No decomp. Deep reddish-violet bordering on purple (Found : Br, 22·6%).

Again the 4-bromo-compound gives the deepest, and the 6-bromo-compound the lightest claret shade. These colours are as deep as those of the corresponding hydroxy-compounds. The hydroxyl groups of the latter therefore have no effect on the colour.

4 : 6-*Dibromo*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Dull brick-red needles, m. p. 259—260° (decomp.). Colour fades at 200°. Deep reddish-violet (Found : Br, 38·0. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·5%).

2 : 4 : 6-*Tribromo*-3-*hydroxybenzaldehyde*-p-*nitrophenylhydrazone :* Deep brick-red needles, m. p. 229—230° (decomp.). Deep reddish-violet.

CXXIII.—*The Hydrolysis of Iodine as Measured by the Iodine Electrode.*

By HUMPHREY DESMOND MURRAY.

To account for the hydrolysis of iodine in aqueous solution, it is convenient to postulate some degree of dissociation. The simplest case is the production of two oppositely charged ions from the diatomic iodine molecule. Hydrolysis follows from the reaction :

$$I^{\cdot} + H_2O = H^{\cdot} + HIO.$$
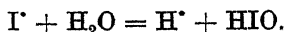
In solution there is, then, between the iodine and hypoiodous acid molecules and the ions $H^{\cdot}$, $I^{\cdot}$, I', and I_3', an equilibrium which is derivable from the mass-action laws : $[I^{\cdot}][I']/[I_2] = K_1$; $[I'][I_2]/[I_3']$ $= K_2$; $[I^{\cdot}][OH']/[HIO] = K_3$. Hence under conditions where any hydrogen iodide formed is largely dissociated,

$$K_1 = \frac{[I']^2}{[I_2]} \cdot \frac{1 + 1/K_2 \cdot [I_2]}{1 + K_w/K_3 \cdot 1/[H^{\cdot}]} \quad \cdot \quad \cdot \quad (1)$$

The object of this investigation was to determine, so far as possible, the value of K_1 by means of an iodine-iodide electrode. It was necessary that the solutions to be examined should be acid, in order to repress the formation of the iodate ion; and with the object of eliminating liquid junction potential differences, a mercurous sulphate electrode was adopted as a reference electrode. This made desirable a determination of the *E.M.F.* of this electrode against the hypothetical normal hydrogen electrode, or failing this, against the iodine electrode, for which accurate values have been recorded. The method adopted was to determine the normal electrolytic potential for the iodine electrode in $N/10$-potassium chloride against the $N/10$-calomel electrode, and then, employing concentrations of iodine and iodide of a similar order, measure the potential difference between the iodine electrode and the mercurous sulphate electrode.

The value of K_2 has been determined with considerable accuracy at different temperatures, but it was thought advisable to redetermine it for solutions containing potassium chloride and sulphuric acid. To this end, solutions of iodine in carbon tetrachloride were shaken with solutions of potassium iodide in $N/10$-potassium chloride and in $N/10$-sulphuric acid until the distribution of iodine between the two layers was constant. Preliminary determinations gave the values 84·1 and 81·9 for the distribution coefficients of iodine at 25° between carbon tetrachloride and $N/10$-potassium chloride and $N/10$-sulphuric acid, respectively, over a range of 0·0006—0·00004 mol./litre in the aqueous layer. Both methods

gave the same value for K_2 at 25° within the limits of experimental error : 0.001390 ± 0.000002. This is higher by about 0.000010 than the accepted value for pure aqueous solutions.

To determine the normal potential of the iodine electrode, successive weighed quantities of pure dry potassium iodide were dissolved in $N/10$-potassium chloride, and the resulting solution was shaken with iodine several times sublimed. The amount of iodine taken up was controlled to a certain extent by the length of time for which the solution was shaken. The iodine solutions were filtered through glass wool into the electrode vessels, and a portion was removed and titrated against thiosulphate. The electrodes were of platinum foil very slightly coated with platinum black. Measurements were made after the $E.M.F.$ had been constant for about an hour. The results are given in Table I : C is the concentration of the potassium iodide added, in mols./litre ; A, the total concentration of iodine found by titration, i.e., $[I_2] + [I_3']$, in mols./litre ; a, the activity coefficient of the iodide ion interpolated from Lewis's results (" Thermodynamics," Lewis and Randall, 1923). The concentrations of free iodine and iodide ion are calculated from the tri-iodide equilibrium.

TABLE I.

Pt. $x\mathrm{I}_2|y\mathrm{KI} + N/10\text{-}\mathrm{KCl}|N/10\text{-}\mathrm{KCl}|\mathrm{Hg}_2\mathrm{Cl}_2 . \mathrm{Hg}.$ Temp. 25°.

$A \times 10^4$.	$C \times 10^3$.	$[I_2] = x$.	$[I'] = y$.	a.	E.		E^0.
5·707	6·764	0·0001032	0·006296	0·790	(a)	0·3039	0·6207
					(b)	0·3036	0·6204
4·304	6·764	0·0000767	0·006410	,,	(a)	0·2990	0·6201
					(b)	0·2996	0·6207
4·373	2·073	0·0001891	0·001825	0·793	(a)	0·3433	0·6206
					(b)	0·3430	0·6203
2·232	2·073	0·0000931	0·001943	,,	(a)	0·3325	0·6205
					(b)	0·3321	0·6201
					Mean		0·6204

$$E^0 = E' - \frac{0.05911}{2} \log \frac{[I_2]}{a^2[I']^2} \quad . \quad . \quad . \quad (2)$$

E is the actual $E.M.F.$ found, referred to the $N/10$-calomel electrode. E' is the potential of the iodine electrode referred to the normal hydrogen electrode, i.e., E increased by 0·3351 volt, the value adopted by Lewis as the difference between the two. E^0 is the normal potential calculated from these results. Its mean value is 0·6204 volt. Lewis (op. cit.) quotes three determinations of this value, one recalculated from data given by Maitland (Z. Elektrochem., 1906, 12, 263) and two by Lewis and Faragher (unpublished work) and Gerke (J. Amer. Chem. Soc., 1922, 44, 1682). If these are made applicable to the free iodine electrode by adding 0·0849 volt, they become 0·6212, 0·6210, and 0·6202, respectively.

The mercurous sulphate required for the electrode was prepared electrolytically.   The $N/10$-sulphuric acid (10 litres) was standardised with sodium carbonate, and the same solution was used throughout.   As a check on the preparation, the mean value of the $E.M.F.$ of the mercurous sulphate electrode measured against the hydrogen electrode in $N/10$-sulphuric acid was determined and found to be $E = 0.7550$ volt.   The value obtained by Lewis and Lacey ($J. Amer. Chem. Soc.$, 1914, **36**, 804) is $E = 0.7546$ volt.

The iodine solutions were prepared as before, but the potassium iodide was dissolved in $N/10$-sulphuric acid.   The results are given in Table II.

TABLE II.

Pt. $x\mathrm{I}_2|y\mathrm{KI} + N/10\text{-}\mathrm{H}_2\mathrm{SO}_4|N/10\text{-}\mathrm{H}_2\mathrm{SO}_4|\mathrm{Hg}_2\mathrm{SO}_4 . \mathrm{Hg}$.   Temp. 25°

$A \times 10^4$.	$C \times 10^3$.	$[\mathrm{I}_2] = x$.	$[\mathrm{I}'] = y$.	a.	E.	E''.
38·52	29·13	0·0001990	0·02333	0·772	(a) 0·0688	0·6829
					(b) 0·0686	0·6827
4·993	3·163	0·0001645	0·002828	,,	(a) 0·0171	0·6829
					(b) 0·0165	0·6823
2·729	2·625	0·0000988	0·002451	,,	(a) 0·0198	0·6827
					(b) 0·0201	0·6830
1·239	2·401	0·0000476	0·002322	,,	(a) 0·0284	0·6833
					(b) 0·0286	0·6835
					Mean	0·6829

$$(E'' + E) = E^0 + \frac{0.05911}{2} \log \frac{[\mathrm{I}_2]}{a^2[\mathrm{I}']^2} \quad . \quad . \quad . \quad (3)$$

E is the actual $E.M.F.$ measured. E'' is the potential of the mercurous sulphate electrode prepared with $N/10$-sulphuric acid, calculated from E and referred to the normal hydrogen electrode. The mean value is $E'' = 0.6829$ volt.   The value calculated from (isohydric) data recorded by Noyes and Stewart ($J. Amer. Chem. Soc.$, 1910, **32**, 1133), taking their mean value for the hydrogen-ion concentration in $0.05M$-acid—0.0585, is 0.6820 volt.

The value of the potential of the iodine electrode in acid solution was now measured.   Pure powdered iodine which had been sublimed several times was shaken with successive quantities of $N/10$-sulphuric acid, the solution filtered through glass wool into the electrode vessel, and a portion removed and titrated.   To obtain reproducible results, it was found necessary to wash the electrodes very thoroughly if they had been previously used in potassium iodide solutions. By combining equations (1) and (2) there is obtained the expression,

$$\log K_1\left(1 + \frac{K_w}{K_3} \cdot \frac{1}{[\mathrm{H}^{\cdot}]}\right) =$$

$$\frac{2}{0.05911}(E^0 - E'' - E) + \log \frac{1}{a^2}(1 + 1/K_2 . [\mathrm{I}_2]),$$

which may be written

$$\log B = \frac{2}{0.05911}(E_x - E) + \log (1 + 1/K_2 . [\mathrm{I}_2]) \quad . \quad . \quad (4)$$

where $B = K_1\left(1 + \dfrac{K_w}{K_3} \cdot \dfrac{1}{[\mathrm{H}^{\boldsymbol{\cdot}}]}\right)$ and $E_x = -0.0559$. The values of a used in calculating the electrode potentials were obtained by interpolation from Lewis's values for the activity coefficient. They have been employed to facilitate comparison with his experimental work, but reference to equations (3) and (4) will show that, if measurements are made in such a solution that we may give to a the value assigned to it in obtaining E'', then the calculated concentration of the iodide ion, and hence of the quantity B, is independent of the value given to a. In calculating B on the basis of the mass action laws, we make the assumption, which appears to be approximately true, that the iodide ion is completely dissociated in $N/10$-sulphuric acid. The results are given in Table III.

TABLE III.

Pt. $x\mathrm{I}_2|y\mathrm{KI} + N/10\text{-}\mathrm{H}_2\mathrm{SO}_4|N/10\text{-}\mathrm{H}_2\mathrm{SO}_4|\mathrm{Hg}_2\mathrm{SO}_4 \cdot \mathrm{Hg}.$

$A \times 10^5$.	E.	$B \times 10^8$.	$A \times 10^5$.	E.	$B \times 10^3$.
81·57	(a) 0·1880	0·89	9·06	(a) 0·1818	0·97
	(b) 0·1872	0·95		(b) 0·1818	0·97
27·19	(a) 0·1849	0·84	4·08	(a) 0·1793	1·14
	(b) 0·1843	0·89		(b) 0·1795	1·12
				Mean	0·97

A constant value for B is obtained, except in the most dilute solution. Now by combining the equations $[\mathrm{I}^{\boldsymbol{\cdot}}][\mathrm{I}']/[\mathrm{I}_2] = K_1$ and $[\mathrm{I}^{\boldsymbol{\cdot}}][\mathrm{OH}']/[\mathrm{HIO}] = K_3$ we find,

$$K_1 K_w/K_3 = [\mathrm{HIO}][\mathrm{H}^{\boldsymbol{\cdot}}][\mathrm{I}']/[\mathrm{I}_2],$$

the value of which is 3×10^{-13} (Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 932). $K_1 K_w/K_3 \cdot 1/[\mathrm{H}^{\boldsymbol{\cdot}}]$, therefore, is of the order 10^{-12}, and ignoring it compared with the value of K_1, we can write,

$$K_1 = 0.97 \times 10^{-8} \text{ at } 25°.$$

By substituting Bray's value in the expression above, we obtain in addition,

$$K_3 = 3.2 \times 10^{-10} \text{ at } 25°.$$

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CXXIV.—*The Condensation of β-Chloro- and β-Ethylcarbonato-propionitriles with Resorcinol.*

By ERNEST CHAPMAN and HENRY STEPHEN.

UNTIL recently, the only limitation of Hoesch's method (*Ber.*, 1915, **48**, 1122) for the preparation of aromatic hydroxy-ketones was its inapplicability to phenolic compounds other than resorcinol,

orcinol, or phloroglucinol. Several cases are now on record, however, in which certain types of nitriles display exceptional behaviour. Cinnamonitrile and phloroglucinol in presence of hydrogen chloride yield 5 : 7-dihydroxy-4-phenyl-3 : 4-dihydrocoumarin (Fischer and Nouri, *Ber.*, 1917, **50**, 693; compare Stephen, J., 1920, **117**, 1531) instead of 2 : 4 : 6-trihydroxyphenyl styryl ketone, which would be expected, the reaction recalling the formation of 7-hydroxy-4-phenylcoumarin from benzacetodinitrile and resorcinol under similar conditions (von Meyer, *J. pr. Chem.*, 1903, **67**, 342; Sonn, *Ber.*, 1918, **51**, 821). Acylacetonitriles of the type $R \cdot CO \cdot CH_2 \cdot CN$ also yield coumarin derivatives (Sonn, *ibid.*, p. 1829; compare also Bargellini and Forli-Forti, *Gazzetta*, 1911, **41**, 747). Again, condensation between β-chloropropionitrile and resorcinol takes place almost exclusively by loss of hydrogen chloride (Langley and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2320), the final product being β-2 : 4-dihydroxyphenylpropionic acid (I) (dihydroumbelliferic acid).* The present authors had begun an investigation on similar lines two months before the publication of Langley and Adams's paper, the object being a synthesis of 7-hydroxychromanone analogous to that of 5-hydroxycoumaranone from chloroacetonitrile and resorcinol by Sonn (*Ber.*, 1917, **50**, 1262).

The first experiments indicated that the chromanone was not formed during the condensation and confirmed the results obtained by Langley and Adams (*loc. cit.*). Further investigation showed that, in addition to β-2 : 4-dihydroxyphenylpropionic acid, β-2 : 6-dihydroxyphenylpropionic acid (II) (which gave the corresponding lactone), 2 : 4-dihydroxyphenyl β-2 : 4-dihydroxyphenylethyl ketone (III), and 2 : 4-dihydroxyphenyl β-2 : 6-dihydroxyphenylethyl ketone (IV) were produced.
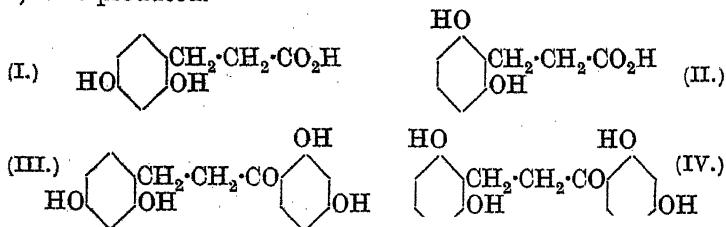
The formation of β-2 : 6-dihydroxyphenylpropionic acid (II) due to the substitution of a hydrogen atom in the vicinal position of resorcinol is remarkable. Apparently the only other instance of such substitution is the formation of 2 : 6-dihydroxybenzoic acid along with 2 : 4-dihydroxybenzoic acid from resorcinol and ammonium

* Langley and Adams have also shown that γ-chlorobutyronitrile behaves similarly, yielding γ-2 : 4-dihydroxyphenylbutyric acid.

carbonate (Senhöfer and Brunner, *Wein Akad. Wiss.*, 1879, **80**, 504; Brunner, *Annalen*, 1906, **351**, 313; compare Zehenter, *ibid.*, 1881, **84**, 341). Langley and Adams did not obtain the compounds (II), (III) and (IV). The ketones are interesting, since they are isomeric with phloretin and dihydrobutein.

The behaviour of β-chloropropionitrile in condensation with resorcinol offers an explanation of the cases cited above. The nitriles referred to are unsaturated and it is probable that the first reaction is the addition of hydrogen chloride, the resulting β-chloro-compound then reacting like β-chloropropionitrile. Langley and Adams also refer to this point and show that acrylonitrile behaves similarly to β-chloropropionitrile in condensation with resorcinol.

In view of the fact that Sonn and Falkenheim (*Ber.*, 1922, **55**, 2983) have synthesised fisetol from ethylcarbonatoacetonitrile and resorcinol, another attempt was made to synthesise 7-hydroxy-chromanone from β-ethylcarbonatopropionitrile and resorcinol. The results were in general the same as in the previous experiments with β-chloropropionitrile.

The experimental work has shown that three cases may be distinguished in condensations of the nitriles with resorcinol in presence of hydrogen chloride : (1) equimolecular quantities of β-chloro-propionitrile and resorcinol gave the acid (I) (yield about 71% of the theoretical) and a small quantity of the acid (II); (2) β-chloro-propionitrile (1 mol.) and an excess of resorcinol (4 mols.) gave the compounds (I), (II), (III) and (IV), the yield of (I) being smaller than in the previous case; (3) equimolecular quantities of β-ethyl-carbonatopropionitrile and resorcinol gave all four compounds as in (2). The following scheme indicates the course of the reactions in cases (1) and (2) :

$$CH_2Cl\cdot CH_2\cdot CN \xrightarrow{+HCl} (V.)\ CH_2Cl\cdot CH_2\cdot CCl{:}NH \xrightarrow{+\ resorcinol}$$
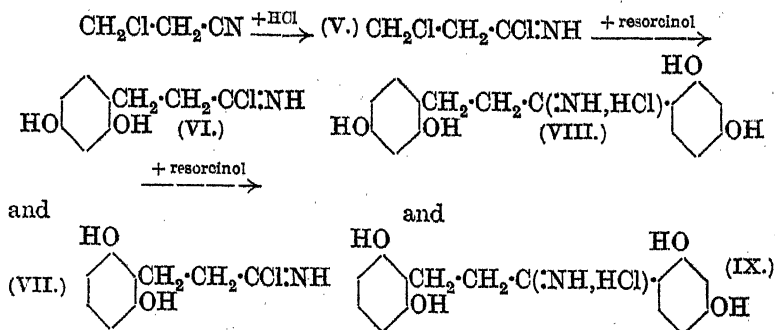
The iminochlorides (VI) and (VII) on hydrolysis gave the acids (I) and (II), respectively. In case (2), interaction between a portion of each iminochloride and excess of resorcinol, following the usual

course of Hoesch's reaction, gave the ketimine hydrochlorides (VIII) and (IX) respectively, from which the corresponding ketones (III) and (IV) were obtained.

Case (3) also may be explained by the above scheme, but it is first necessary to consider the action of hydrogen chloride on β-ethylcarbonatopropionitrile. The experiments show that the following reactions take place :

$$\text{EtO}_2\text{C·O·CH}_2\text{·CH}_2\text{·CN} \xrightarrow{\text{HCl}} \text{(X.)} \ \text{EtO}_2\text{C·O·CH}_2\text{·CH}_2\text{·CCl:NH} \xrightarrow{\text{HCl}}$$
$$\text{CH}_2\text{Cl·CH}_2\text{·CCl:NH} \ \text{(v.)} + \text{EtOH} + \text{CO}_2.$$
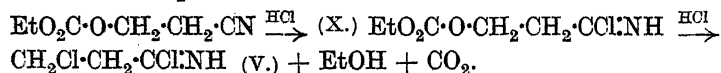
The alcohol formed was shared between the iminochlorides (X) and (V), giving a mixture of the hydrochlorides of β-ethylcarbonato-propioiminoethyl ether, $\text{EtO}_2\text{C·O·CH}_2\text{·CH}_2\text{·C(OEt):NH,HCl}$, and β-chloropropioiminoethyl ether, $\text{CH}_2\text{Cl·CH}_2\text{·C(OEt):NH,HCl}$. The composition of the mixture was determined by hydrolysis, which gave ethyl β-ethylcarbonatopropionate and ethyl β-chloropropionate. The same reactions evidently took place in case (3), because the same two esters were isolated. The formation of the above ethers diminished the concentration of β-chloropropioimino-chloride (V), and the resorcinol being now in excess the condensation proceeded as in case (2).

EXPERIMENTAL.

β-*Chloropropionitrile.*—To a solution of 28 g. of ethylene cyanohydrin in 30 c.c. of chloroform cooled in ice and salt, 50 g. of thionyl chloride were added gradually with shaking. After an hour, the chloroform was evaporated and the residue of brown oil distilled under diminished pressure. The nitrile was obtained as a colourless liquid, b. p. 85—87°/20 mm.; 173—174·5° at ordinary pressure (Henry, *Bull. Acad. roy. Belg.*, 1898, **35**, 360, gives b. p. 174—176°/752 mm.).

β-*Ethylcarbonatopropionitrile.*—Ethyl chloroformate (170 g.) was added during 2 hours with vigorous shaking to a solution of ethylene cyanohydrin (85 g.) in dry pyridine (220 g.) cooled with water. After 12 hours, the deep red solution was acidified with 130 c.c. of concentrated hydrochloric acid diluted with 500 c.c. of water, care being taken to avoid rise in temperature. A heavy oil separated which was dissolved in ether, dried, and, after removal of the solvent, fractionated under diminished pressure, 123 g. of the nitrile being obtained (yield 72%), b. p. 127—128°/15 mm., 206°/760 mm. [Found : C = 50·3, 50·2 ; H = 6·6, 6·3 ; N (Kjeldahl) = 9·7, 9·6. $\text{C}_6\text{H}_9\text{O}_3\text{N}$ requires C = 50·3 ; H = 6·3 ; N = 9·8%]. The nitrile was a colourless liquid which did not solidify at —20° ; it was heavier than water, in which it was almost insoluble, and was readily hydro-

lysed by the action of acids and alkalis, the ethylcarbonato-group being decomposed simultaneously with the nitrile group.

Action of Hydrogen Chloride on β-Ethylcarbonatopropionitrile.— Dry hydrogen chloride was passed for 5 hours into a well-cooled solution of the nitrile (50 g.) in dry, alcohol-free ether (75 c.c.). After 12 hours, the addition of 125 c.c. of dry ether caused the separation of a white crystalline mass, which was washed several times with dry ether and dried over caustic potash. Yield 36 g. No suitable solvent could be found for crystallising the solid, which melted at 102—103° (decomp.). From the analytical results (Found : C = 40·9, 41·1; H = 7·5, 7·6; N = 6·7, 6·6; Cl = 22·9, 23·0) it appeared improbable that the solid was β-ethylcarbonatopropioiminochloride, $EtO_2C \cdot O \cdot CH_2 \cdot CH_2 \cdot CCl \colon NH$ (Calc., C = 40·1; H = 5·6; N = 7·8; Cl = 19·8%). It was readily soluble in water giving a clear solution, slightly acid to litmus, which on warming deposited globules of oil. The solid evolved ethyl chloride a few degrees above its m. p., and gave ammonia on treatment with dilute sodium hydroxide solution. These properties are characteristic of the hydrochloride of an iminoethyl ether (compare Pinner and Klein, *Ber.*, 1877, **10**, 189).

The colourless oil which separated on warming an aqueous solution of the solid (25 g. in 30 c.c.) was dissolved and dried in ether. The neutral liquid (18 c.c.) remaining after removal of the solvent was separated into two fractions, b. p. 160—170° (3 c.c.) and 229—231° (10 c.c.). The former consisted of ethyl β-chloropropionate (b. p. 162—163°) (Found : C = 43·4; H = 6·6; Cl = 25·3. Calc., C = 43·9; H = 6·6; Cl = 26·0%); the latter was *ethyl β-ethylcarbonatopropionate* (Found : C = 50·7, 50·4; H = 7·5, 7·6. $C_8H_{14}O_5$ requires C = 50·5; H = 7·4%), a colourless neutral liquid, b. p. 230°, which is slowly hydrolysed by cold dilute sodium hydroxide solution.

It is therefore justifiable to conclude that the solid consisted of a mixture of the hydrochlorides of β-chloropropioiminoethyl ether and β-ethylcarbonatopropioiminoethyl ether, which on hydrolysis would give the above esters.

Condensation of Resorcinol and β-Chloropropionitrile.—(1) Using equimolecular quantities. The method and conditions employed were similar to those described by Langley and Adams (*loc. cit.*), but a higher yield was obtained (71%), 11 g. of resorcinol and 9 g. of the nitrile giving 13 g. of β-2 : 4-dihydroxyphenylpropionic acid, m. p. 165° (Found : C = 59·5; H = 5·5. Calc., C = 59·3; H = 5·5%). During the crystallisation of the crude acid from hot water a small quantity of β-2 : 6-dihydroxyphenylpropionic acid (see next section) separated first from solution. β-2 : 4-Dihydr-

oxyphenylpropionic acid is only slightly soluble in hot benzene or chloroform, but readily soluble in most other solvents. The aqueous solution gave an indigo-blue coloration with ferric chloride, and reduced ammoniacal silver nitrate in the cold and Fehling's solution on warming. Acetylation of the acid with acetic anhydride gave 7-*acetoxy*-3 : 4-*dihydrocoumarin*, transparent prisms from alcohol, m. p. 111—111·5° (Found : C = 64·0; H = 4·9. $C_{11}H_{10}O_4$ requires C = 64·0; H = 4·9%). Hydrolysis of the coumarin with dilute hydrochloric acid gave the above acid. The latter on heating for 2 hours at 125—130° was converted into the lactone, 7-*hydroxy*-3 : 4-*dihydrocoumarin* (dihydroumbelliferone), flat plates from toluene, m. p. 133—134° (Found : C = 66·0; H = 4·8. $C_9H_8O_3$ requires C = 65·9; H = 4·9%). Acetylation gave the acetyl compound described above.

(2) Using excess of resorcinol. A solution of 11·5 g. (1 mol.) of β-chloropropionitrile and 56 g. (4 mols.) of resorcinol in 200 c.c. of dry ether was cooled in ice and salt and saturated with hydrogen chloride. Zinc chloride was not used. The method of treating the reaction product was similar to that described in the next section, except that distillation with steam was omitted. Reference only need be made here to the compounds isolated, as these are described later, namely, β-2 : 4-dihydroxyphenylpropionic acid (12 g.), β-2 : 6-*dihydroxyphenylpropionic acid* (3·8 g.) and β-2 : 4- and β-2 : 6-*dihydroxyphenylethyl* 2 : 4-*dihydroxyphenyl ketones* (1·8 g. and 0·5 g. respectively).

Condensation of β-Ethylcarbonatopropionitrile and Resorcinol.— A rapid stream of hydrogen chloride was passed for 5 hours into a well-cooled solution of resorcinol (1·1 mols.; 60 g.) and the nitrile (1 mol.; 70 g.) in dry ether (200 c.c.). After remaining a week in an ice-chest, a red oil and a thick, crystalline deposit had formed, the quantity of which increased on the addition of 200 c.c. of dry ether. The ether layer was decanted from the oil and crystalline deposit, which were washed with a little ether and dissolved in 220 c.c. of water. From the red solution, on warming for a few minutes, an oil separated which was distilled with steam and proved to be a mixture of ethyl β-ethylcarbonatopropionate and ethyl β-chloropropionate (compare p. 889). The red solution remaining after steam distillation deposited a thick red oil mixed with a small amount of a pale yellow crystalline material. Both were removed with ether, and the aqueous solution was evaporated to dryness, leaving 23 g. of ammonium chloride containing no appreciable amount of organic matter. The ether extract was shaken with 600 c.c. of saturated aqueous sodium bicarbonate, and the aqueous layer (A), which had acquired a reddish-purple colour, was separated,

the ether layer being washed with a little water, dried, and the ether removed on the water-bath. A red oil remained, which gradually set to a crystalline mass (B) when cold. The aqueous layer (A) was acidified with hydrochloric acid, the colour changing from purple to yellow with deposition of a pale yellow, crystalline powder. This, crystallised from hot water with the addition of animal charcoal, gave 5 g. of β-2 : 6-dihydroxyphenylpropionic acid (see below). The filtrate was concentrated to a quarter of its bulk and extracted with ether; after removal of the solvent β-2 : 4-dihydroxyphenyl-propionic acid (16·5 g.) remained.

β-2 : 6-*Dihydroxyphenylpropionic acid* crystallised from hot water in glistening, prismatic needles, which melted and decomposed at 174—176°, resolidified at 178°, and melted again at 224—225° (Found : C = 58·9, 59·4; H = 5·4, 5·6. $C_9H_{10}O_4$ requires C = 59·3; H = 5·5%). A solution of the acid in alcohol gave a red coloration with ferric chloride which distinguished it from the isomeric acid. In other respects, it resembled the latter. On fusion at 190° for ½ hour, the corresponding lactone, 5-*hydroxy*-3 : 4-*dihydrocoumarin*, was obtained; it formed snow-white prisms, m. p. 224—225°, from alcohol after treatment with charcoal (Found : C = 65·7; H = 5·1. $C_9H_8O_3$ requires C = 65·9; H = 4·9%). It is sparingly soluble in cold and moderately soluble in hot water, from which it crystallises unchanged. It differs from its isomeride in being slightly soluble in boiling toluene. It is insoluble in sodium bicarbonate solution, but soluble in cold dilute sodium hydroxide, and the lactone was recovered unchanged on acidifying the solution immediately. On warming, the alkaline solution became orange-coloured and after acidification the corresponding acid was precipitated. An alcoholic solution of the lactone gave a reddish-brown coloration with ferric chloride. The formation of the lactone was taken as conclusive evidence for the formula of the acid.

The crystalline mass (B) was stirred with 15 c.c. of water, the greater part dissolving, leaving a residue of fine yellow needles (6·5 g.). The filtrate from the latter was evaporated, leaving 22 g. of unchanged resorcinol. The yellow crystalline residue was extracted successively with 200, 200, and 250 c.c. of boiling water. The residue (1 g.) after the third extraction was 2 : 4-*dihydroxyphenyl* β-2 : 6-*dihydroxyphenylethyl ketone*, which on crystallising from alcohol with the addition of charcoal was obtained in fine white needles, m. p. 228—229° (Found : C = 65·5, 65·6; H = 5·2, 5·1. $C_{15}H_{14}O_5$ requires C = 65·7; H = 5·1%). There was insufficient material for the preparation of derivatives. The ketone was only slightly soluble in hot water, readily soluble in hot alcohol or acetic

acid, the alcoholic solution giving a reddish-brown coloration with ferric chloride. It dissolved in aqueous sodium hydroxide and was recovered unchanged after boiling and acidifying the red solution. This behaviour distinguished the ketone definitely from the lactone of β-2 : 6-dihydroxyphenylpropionic acid. A mixture of the two melted at 208—211°.

2 : 4-*Dihydroxyphenyl* β-2 : 4-*dihydroxyphenylethyl ketone* was deposited from the first of the aqueous extracts * above in diamond-shaped plates (4 g.), which lost 2 mols. of water at 100°, the anhydrous compound melting at 186° (Found : in material dried in a vacuum for 30 hours or 4 days, loss at 110° = 11·6, 11·7 : in the anhydrous substance, C = 65·8, 65·5; H = 5·2, 5·1. $C_{15}H_{14}O_5, 2H_2O$ requires $H_2O = 11·6\%$. $C_{15}H_{14}O_5$ requires C = 65·7; H = 5·1%). The ketone, unlike the isomeride above, was readily soluble in hot water, and insoluble in benzene, ligroin, or chloroform. An alcoholic solution gave a reddish-brown coloration with ferric chloride. The *phenylhydrazone* was obtained by warming the anhydrous ketone (0·9 g.) with excess of phenylhydrazine (1·25 g.), and after crystallisation from alcohol was obtained in pale brown needles, m. p. 214—215° (Found : N = 7·9, 7·8. $C_{21}H_{20}O_4N_2$ requires N = 7·7%).

In conclusion, one of us (E. C.) desires to express his thanks to the Trustees of the Sir Clement Royds Memorial Scholarship, during the tenure of which a portion of the above work was completed.

CXXV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part X. The Action of Hydrazine Hydrate on the Halogen Derivatives of α-Nitro-fatty Acids.*

By ALEXANDER KILLEN MACBETH and DAVID TRAILL.

THE investigations (J., 1922, **121**, 892, and subsequent papers) on the influence of various groups on the reactivity of halogen compounds towards reducing agents—notably hydrazine hydrate—have been supplemented by a study of derivatives of representative α-nitro-fatty acids. Substances containing the structures ·CO·CHX·CO·, ·CO·CX₂·CO·, ·CO·CHX·CO₂Et, ·CO·CX₂·CO₂Et, EtO₂C·CRX·CO₂Et, EtO₂C·CX₂·CO₂Et (where X represents a halogen atom) have already been examined, and it seemed of

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* The second extract deposited a small quantity of the previous ketone.

interest to prepare compounds of the types $O_2N \cdot CRX \cdot CO_2Et$, $O_2N \cdot CX_2 \cdot CO_2Et$ for comparison.

Two main views have been advanced to account for the reactivity of the halogen atoms in compounds of the types we have examined, one based on the tautomeric hydrogen hypothesis (Burton and Kenner, J., 1922, **121**, 489 : see also Thole and Thorpe, J., 1911, **99**, 2183; Norris and Thorpe, J., 1921, **119**, 1203), the other on the polarity of the oxygen atoms. Opinions have been expressed (Robinson, *Ann. Reports*, 1922, **19**, 102; Allsop and Kenner, J., 1923, **123**, 2296) that both factors may in different cases contribute to the observed reactivities, and apparently contradictory observations may be accounted for on such grounds. The chief outstanding cases in which direct polarity effects leading to a "positive" halogen cannot be traced are the tetrahalogen derivatives of methane. Nef (*Annalen*, 1899, **308**, 329) and Gustavson (*ibid.*, 1874, **172**, 173) have shown that such substances are converted into trihalogenomethanes by a variety of alkaline reducing agents, and further examples of similar effects have been recorded by Griffith and Hunter (J., 1924, **125**, 463). We now find that the action of hydrazine hydrate on tetrabromomethane results in reduction, the removal of one of the bromine atoms, and the liberation of the corresponding volume of nitrogen. The consideration of steric effects (Chattaway and Harrison, J., 1916, **109**, 171) would appear to furnish the most satisfactory explanation of the lability of the halogen atom in these cases.

The present results support those obtained in our previous work, hydrazine hydrate displaying, in the case of the α-nitro-fatty acids now examined, its capacity of differentiating between the reactivities of chlorine and bromine atoms in compounds of precisely similar structure.

The reactivity of chlorotrinitromethane is much less than that of the corresponding bromo-compound, although reduction occurs in both cases (Macbeth and Pratt, J., 1921, **119**, 1356). More striking effects are found in the case of certain diketones, no reduction occurring in such derivatives as 4 : 4-dichloro-1 : 1-dimethyl-*cyclo*hexane-3 : 5-dione and *cyclo*hexane*spiro*-4 : 4-dichloro*cyclo*hexane-3 : 5-dione, whereas nitrogen is readily liberated when the corresponding dibromo- and chlorobromo-compounds are treated with hydrazine hydrate, one bromine atom being removed by the reducing agent in each case. In agreement with these observations, all the chloro-derivatives of the α-nitro-fatty acids examined are unacted upon by hydrazine hydrate, whereas bromine is readily removed from the corresponding bromo- and chlorobromo-compounds.

These effects seem to us to be best explained on a polarity basis. It might be urged that the desire to acquire a tautomeric hydrogen atom, or the operation of steric influences, may equally well be the factor governing the lability of the halogen atom in such compounds as dibromonitroacetic, bromonitropropionic and bromonitrobutyric esters. But such an explanation is considerably weakened when it is seen that the corresponding chloro-compounds are not reactive under the same experimental conditions : and it is still more difficult to reconcile the reactivity of bromonitroacetic ester with views other than those developed on polarity considerations. The behaviour of the latter compound falls into line with the reactivities of the monohalogen derivatives of malonic and acetoacetic esters; and since these compounds already possess a hydrogen atom attached to the α-carbon atom, the tautomeric hydrogen hypothesis is inapplicable, and the development of spatial effects is not to be expected.

The properties of the nitro-fatty acids would appear to suggest that the influence of the nitro-group in inducing reactivity of the halogen atom is less than that of a ketonic or carbethoxyl group, as will be seen in the following examples.

Halogen reduced by hydrazine.	Halogen not reduced.
$R \cdot CO \cdot CHCl \cdot CO_2Et$	
$R \cdot CO \cdot CRCl \cdot CO_2Et$	
$R \cdot CO \cdot CCl_2 \cdot CO_2Et$	$O_2N \cdot CHCl \cdot CO_2Et$
$EtO_2C \cdot CHCl \cdot CO_2Et$	$O_2N \cdot CRCl \cdot CO_2Et$
$EtO_2C \cdot CRCl \cdot CO_2Et$	$O_2N \cdot CCl_2 \cdot CO_2Et$
$EtO_2C \cdot CCl_2 \cdot CO_2Et$	
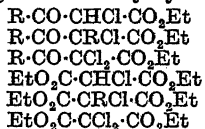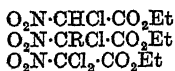
Support for this view is found on comparing the properties of the bromine atom in ethyl bromonitroacetate and bromodinitromethane : the former is readily reduced by hydrazine at the ordinary temperature, whereas the latter is unaffected (Macbeth and Pratt, *loc. cit.*).

EXPERIMENTAL.

The hydrazine reactions were in all cases carried out with a 50% solution of hydrazine hydrate in a Van Slyke nitrometer.

Tetrabromomethane was prepared by Ponzio's method (*Atti R. Accad. Sci. Torino*, 1906, 41, 415). In alcoholic solution it reacted vigorously with hydrazine hydrate, one bromine atom being removed and the corresponding volume of nitrogen liberated. 0·3305 Gram of tetrabromomethane liberated 11·3 c.c. of nitrogen at 14·5° and 756 mm., which corresponds with a 96% reduction.

Nitroacetic Acid Series.

Ethyl Monochloronitroacetate.—Dry ammonia gas was passed into an ethereal solution of ethyl nitroacetate (prepared by Bouveault

and Wahl's method, *Bull. Soc. chim.*, 1904, **31**, 851) and the ammonio-derivative so obtained was chlorinated and brominated as described below.

The chloro-ester was best obtained by passing a slow stream of chlorine into an aqueous solution of the ammonio-derivative for 1 hour. The heavy yellow oil which had separated was extracted with ether, washed with a dilute solution of sodium thiosulphate and with water, dried over anhydrous sodium sulphate, and, after removal of the solvent, distilled under reduced pressure. Ethyl monochloroacetate collected as a main fraction, b. p. 77°/8 mm., n_D 1·4412 (Found : Cl, 21·2. Calc., Cl, 21·2%). The ester was practically unacted upon by hydrazine hydrate, traces only of nitrogen being liberated after upwards of $\frac{1}{2}$ hour.

The *ammonio-derivative of ethyl monochloronitroacetate* was prepared by the action of dry ammonia gas on an ethereal solution of the chloro-ester. It separated as a white, flaky solid, but gradually changed to a compact, yellow precipitate. The compound is fairly stable, but reddens somewhat on exposure to air. It crystallises in long, white needles, m. p. 114—115°, from alcohol. Crystallisation presents a curious appearance under the microscope ; in the thicker parts a mosaic structure forms, with peculiar interference in growth : in other parts rosettes form (Found : Cl, 19·2. $C_4H_9O_4N_2Cl$ requires Cl, 19·3%).

Ethyl dichloronitroacetate gradually separated when a slow stream of chlorine was passed into an aqueous solution of the preceding compound, and was treated as described in the case of the monochloro-compound. It has b. p. 72°/8 mm., n_D 1·4430 (Found : Cl, 35·1. $C_4H_5O_4NCl_2$ requires Cl, 35·15%).

As in the case of the monochloro-ester there is practically no reaction with hydrazine hydrate.

Ethyl Bromonitroacetate.—The ammonio-derivative of nitroacetic ester was gradually added, with occasional shaking, to a solution of bromine (1 mol.) in carbon disulphide. Water was added to dissolve the precipitated ammonium bromide, and the carbon disulphide was thereafter successively washed with a dilute solution of sodium thiosulphate and water. After drying and removal of the solvent, the residual oil was distilled under reduced pressure, when the bromo-ester collected as a main fraction, b. p. 105°/10 mm., $n_D^{16°}$ 1·4798 (Found : Br, 37·6. $C_4H_6O_4NBr$ requires Br, 37·7%).

The ester reacts readily with hydrazine hydrate, nitrogen being liberated and the halogen atom removed by reduction. 2·12 Grams of the bromo-ester were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 12·2 c.c. N_2 at 13·5° and 741·5 mm., which corresponds with complete reduction of the bromo-ester.

The *ammonio-derivative of ethyl bromonitroacetate*, prepared as in the preceding cases, crystallised from alcohol in long, colourless needles, m. p. 134° (decomp.) (Found : NH_3, 7·7. $C_4H_9O_4N_2Br$ requires NH_3, 7·8%).

Ethyl dibromonitroacetate, prepared from the preceding compound by bromination in carbon disulphide solution as previously described, was a colourless liquid, b. p. 97·4°/6 mm., n_D 1·4985 (Found : Br, 54·8. $C_4H_5O_4NBr_2$ requires Br, 55·0%).

The ester reacts vigorously with hydrazine hydrate. 1·455 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of the solution liberated 13 c.c. N_2 at 14·5° and 747 mm., which corresponds with 100% reduction of the dibromo-ester. 5—6 C.c. of the gas were liberated almost immediately, the residual volume collecting in about 5 minutes.

Ethyl chlorobromonitroacetate, prepared by the bromination in carbon disulphide solution of the ammonio-derivative of ethyl chloronitroacetate, was a colourless oil, b. p. 89°/11 mm., n_D 1·4663 (0·1572 of the ester gave 0·212 of silver halides : calc. for $C_4H_5O_4NClBr$, 0·218).

The ester reacts with hydrazine hydrate, the reduction removing only the bromine atom. 1·2325 Grams were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 9·6 c.c. N_2 at 14° and 765 mm., which corresponds with about 83% removal of the bromine atom.

Nitropropionic Acid Series.

The ammonio-derivative of ethyl nitropropionate was prepared by the action of alcoholic ammonia on ethyl nitro*iso*succinate. Some difficulty was experienced at first in obtaining a good yield of ethyl nitro*iso*succinate by Steinkopf and Supan's method (*Ber.*, 1910, 43, 3245), but this was probably due to imperfect decomposition of the acetic anhydride in the later stages, and in subsequent experiments better yields were obtained when the mixture after reaction was shaken by mechanical means for upwards of an hour with 2 litres of cold water.

Attempts to prepare ethyl nitropropionate by the direct nitration of ethyl methylacetoacetate in acetic anhydride gave very low yields of the ester.

Ethyl-α-chloronitropropionate was obtained in good yield by passing a stream of chlorine into an aqueous solution of the ammonio-derivative of the nitro-ester; after about 30 minutes, most of it separated as a pale green oil. After the usual treatment the ester was obtained as a colourless oil, b. p. 80°/9 mm., n_D 1·4301 (Found : Cl, 19·1. $C_5H_8O_4NCl$ requires Cl, 19·55%). The ester is practically unacted upon by hydrazine hydrate,

only a small volume of nitrogen being liberated at the laboratory temperature.

Ethyl α-bromonitropropionate, prepared by bromination of the ammonio-derivative of the nitro-ester by a precisely similar method to those already described, was a clear, colourless liquid, b. p. 88°/20 mm., n_D 1·4535 (Found : Br, 35·4. $C_5H_8O_4NBr$ requires Br, 35·6%).

The ester reacts very vigorously with hydrazine hydrate at the ordinary temperature, the nitrogen being all liberated in about 30 seconds. 1·130 Grams of the ester were dissolved in 25 c.c. of alcohol, and 5 c.c. of this solution liberated 11·8 c.c. N_2 at 16° and 764 mm., which corresponds with complete removal of the halogen atom.

Hydrazine Derivative of Ethyl α-Nitropropionate.—During the hydrazine reactions described above, a white solid collected in the reaction vessel. It crystallised from alcohol in long, white, silky needles, m. p. 120°, and proved to be the hydrazine derivative of ethyl α-nitropropionate (Found : N, 23·7. $C_5H_{13}O_4N_3$ requires N, 23·5%).

Rimini's method (*Atti R. Acad. Lincei*, 1906, **15**, ii, 320) for the estimation of hydrazine in a hydrazine salt was modified for use in a Van Slyke nitrometer. A weighed quantity of the hydrazine derivative was washed into the reaction bulb with water, and a measured volume of potassium iodate added. On addition of a known volume of potassium hydroxide solution a vigorous reaction occurred with liberation of nitrogen (Found : N_2H_4, 17·9. $C_5H_{13}O_4N_3$ requires N_2H_4, 17·9%).

Nitrobutyric Acid Series.

Ethyl α-Chloronitrobutyrate.—Ethyl nitrobutyrate was prepared from ethyl ethylacetoacetate by Schmidt and Widman's method (*Ber.*, 1909, **42**, 1895).

The chloronitro-ester was obtained in good yield by chlorination of the freshly prepared ammonio-derivative of the nitro-ester. It is a colourless oil, b. p. 77—79°/6 mm., n_D 1·4338 (Found : Cl, 18·1. $C_6H_{10}O_4NCl$ requires Cl, 18·2%).

As in the case of the other chloro-compounds the reduction of the ester by hydrazine hydrate is negligible.

Ethyl α-bromonitrobutyrate, prepared by bromination of the ammonio-derivative of the nitro-ester in carbon disulphide, had b. p. 83—84°/9 mm., n_D 1·4990 (Found : Br, 33·1. $C_6H_{10}O_4NBr$ requires Br, 33·3%).

The ester reacts vigorously with hydrazine hydrate, the reduction being complete in about 30 seconds. 5 C.c. of an alcoholic solution

containing 4·8% of the bromonitro-ester liberated 11·6 c.c. N_2 at 16° and 767 mm., which corresponds with complete removal of the halogen atom.

CXXVI.—*The Chemistry of Petroleum. Part I. The Occurrence of Compounds of Sulphur in the Light Distillate from the Crude Oil of Maidan-i-Naftun.*

By STANLEY FRANCIS BIRCH and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

THE sulphur that is found in the distillates from all crude petroleums is present as free sulphur, or as sulphur compounds having a highly objectionable odour. The removal of these compounds is of the greatest importance to the refiner, who until recently had no clue as to their identity and who has removed them by purely empirical methods.

The isolation and identification are here described of some of the sulphur compounds present in the first 36% (by volume) of the distillate from crude Persian petroleum, *i.e.*, the fraction from which petrol and kerosene are obtained.

The crude oil itself is obtained from the wells at Maidan-i-Naftun, which is about 140 miles north-north-east of Mohammerah, in south-east Persia. As it issues from the wells it is accompanied by much gas, which consists chiefly of paraffin hydrocarbons together with a large proportion of hydrogen sulphide. The quantity of the latter constituent naturally varies with the pressure of the gas–liquid system from which the sample is taken; in fact, after keeping for some time at atmospheric pressure, the crude oil retains so little hydrogen sulphide that it has only a faint, somewhat sweet odour.

In marked contrast with the crude oil, the sulphur compounds in the distillates have, as stated above, a highly objectionable odour; this alone, we think, is sufficient proof that they are not present as such in the original petroleum, but are formed by decomposition, a conclusion borne out by the behaviour of the crude oil on distillation. When the temperature of the oil reaches about 120°,

elementary sulphur appears in the distillate. Moreover the total content of free and combined sulphur of the earlier fractions may be reduced by distilling the oil in such a way that the temperature is kept as low as possible, for example, by using an ample current of steam. This confirms the hypothesis that the appearance of sulphur compounds in the distillate is preceded by a thermal decomposition in the liquid phase.

The sulphur compounds in the 36% distillate are of two kinds, acidic and neutral. The first class includes hydrogen sulphide and (*vide infra*) mercaptans. The compounds of the second class react with mercuric chloride, but we have not yet examined the additive compound in any detail. Since Waterman and Heimel (*Chem. Weekblad*, 1924, **21**, 374) have reported the absence of thiophen from the distillates from Persian oil, the neutral compounds responsible for the mercuric chloride reaction must presumably be organic sulphides. In the absence of evidence to the contrary, organic disulphides, or carbon disulphide, may likewise be present. The distillate also contains elementary sulphur. In the present research we have investigated the acidic, sulphur-containing constituents of the 36% distillate, because this material is treated with sodium hydroxide solution in the normal course of refining, and a supply of " spent soda solution " was therefore available.

The organic sulphur compounds are readily isolated from " spent soda " by distillation, during which progressive hydrolysis of the sodium mercaptides occurs. This operation does not cause the liberation of hydrogen sulphide. The mercaptans are, in fact, very much weaker acids even than hydrogen sulphide. Thus they are only partly removed from solution in a hydrocarbon by shaking with sodium hydroxide solution, whereas hydrogen sulphide, in an equivalent quantity, is completely extracted. Moreover, apart from distillation or acidification, the mercaptans may be partly isolated from an alkaline solution by dilution, or by shaking with petroleum. This point is of importance in refinery practice, both because the mercaptans are incompletely extracted from petroleum distillates by washing with sodium hydroxide solution, and because the " spent soda " may be partly revivified by boiling.

The mercaptans were isolated from the crude mixture of sulphur compounds by shaking with 50% potassium hydroxide solution and acidifying the aqueous liquid. The material thus obtained was fractionally distilled, yielding about 55—60% of *iso*propyl mercaptan, 18% of *iso*butyl mercaptan, and 9% of fractions of low boiling point which appeared to consist of ethyl mercaptan. Intermediate fractions and the high-boiling residue accounted for the remainder.

We believe ourselves correct in stating that mercaptans have not hitherto been isolated from petroleum. References to these compounds are, of course, scattered throughout the technical literature ;* but an actual separation seems never to have been accomplished.

Owing to its presence in so large a proportion of the total, the identification of *iso*propyl mercaptan, the first of the sulphur compounds which we succeeded in isolating, presented no special difficulty. The fraction of b. p. 56—58° was analysed and various indubitable derivatives of *iso*propyl mercaptan were prepared from it.

The second fraction, b. p. 86—88°, was identified in a similar manner as *iso*butyl mercaptan.

Owing to the small quantity (9%) obtained of the fraction which appeared to be ethyl mercaptan, a pure specimen of this substance could not be isolated. Indications of its presence were nevertheless obtained (see p. 903).

Analysis of the mercurichloride prepared from the fraction of highest boiling point seemed to indicate the presence of a higher mercaptan. By analogy with the lower homologues present, *iso*amyl mercaptan would appear the most likely. Certainly, apart from ethyl mercaptan, normal mercaptans do not appear to be present in the 36% distillate from Persian petroleum ; we seem, in fact, to have a further example of the prevalence, in compounds from natural sources, of the *gem*-dialkyl grouping. It will of course be realised that the structure of the mercaptans found in the distillate is determined by the constitution of the more complex molecule, or molecules, from which they are eliminated during distillation. Without attempting to base any broad generalisation upon the somewhat meagre facts so far elicited, we may suggest that possibly that part of the parent molecule which is eliminated as a mercaptan has originally been formed by the addition of hydrogen sulphide to an ethylenic bond. This would tend to produce a branched chain rather than a normal configuration.

The mercaptans isolated were actually obtained from " spent soda." There was, therefore, an apparent possibility that the normal isomerides, although present in the petroleum distillates, might escape extraction during the soda-washing process owing to their extremely feeble acidity. This explanation of the absence of normal mercaptans from " spent soda " is not correct, however,

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* For example, Engler-Höfer (" Das Erdöl," I, p. 477) quotes a statement by Kwjatkowsky that mercaptans are present in Baku petroleum *(Anleitung z. Verarb. d. Naphta*, 12, 1904, aus Höfer, *Erdöl u. s. Verw.*, 2 Aufl., 82).

Incidentally it should be noted that no mention is made by Engler-Höfer of the presence in petroleum of disulphides.

for in a series of comparative experiments, in which solutions containing equivalent quantities of various mercaptans were extracted by means of a given volume of 5% sodium hydroxide solution, it was found that the normal mercaptans were slightly stronger acids than their respective isomerides. Incidentally, the decrease in acidity with increase in molecular weight was very marked.

The portion of the sulphur compounds from "spent soda" which was insoluble in 50% potassium hydroxide solution consisted of organic disulphides, together with traces of hydrocarbons. It is evident that these compounds, being neutral, could not have been extracted from the petroleum distillate by means of sodium hydroxide solution. They must, in fact, have been formed in the "spent soda" subsequent to the process of extraction. Although at first a complete explanation of their production was not forthcoming, a clue was found in an observation of Böttger (*Annalen*, 1884, **223**, 348); he showed that sodium ethylmercaptide and sulphur, when heated at 100° in presence of ethyl alcohol, give diethyl disulphide and sodium polysulphide. Such drastic conditions are not, however, necessary to bring about the change, since Holmberg (*Annalen*, 1908, **359**, 81) has found that alkali mercaptides react in aqueous solution with free sulphur or an alkali polysulphide to give organic disulphides at the ordinary temperature, an observation which we have confirmed. Wendt and Diggs (*Ind. Eng. Chem.*, 1924, **16**, 1113) are apparently unaware of Holmberg's work on the subject; they state that diethyl disulphide is formed by the action of sulphur on ethyl mercaptan in petroleum solution. The 36% distillate from Persian petroleum certainly contains free sulphur, which might be to some extent the cause of the production of disulphides. The latter would then, however, be found in the petroleum, from which they could not be extracted by sodium hydroxide solution. But actually it is from the "spent soda" that they have been isolated; it is clear, therefore, that the formation of the disulphides must occur in the aqueous layer subsequent to extraction. Moreover, since the "spent soda," previous to being distilled, is free from any visible quantity of oily material, it seems certain that the disulphides are actually formed during the process of distillation. It is probable that the agent responsible for the oxidation is sodium polysulphide, which is invariably present, and imparts to the "spent soda" a pronounced yellow colour. The probability of this explanation has been greatly increased by the observation that, although a moderate increase in temperature does not appreciably affect the velocity with which sodium polysulphide oxidises mercaptans, heating the reaction mix-

ture to its boiling temperature very greatly hastens the production of disulphides. The total quantity of hydrocarbons present as impurity in the mixed disulphides is comparatively small, and we think this material consists simply of traces of the original petroleum distillate, carried mechanically in the spent soda.

The ease with which mercaptans are oxidised to give disulphides is somewhat surprising; the conversion may actually be brought about by passing oxygen, or air, into an aqueous solution of a sodium mercaptide. This result appears the more striking when the comparatively low solubility of oxygen in aqueous solutions is remembered.

The disulphides which have actually been isolated are diethyl disulphide, di*iso*propyl disulphide, and di*iso*butyl disulphide. Appropriate fractions were obtained by distillation, and then examined separately, but owing to the presence of hydrocarbons in these fractions, it was necessary to reduce each fraction to the corresponding mercaptan by means of zinc dust and glacial acetic acid. The mercaptans so obtained were then converted into solid derivatives and analysed or otherwise characterised in this form.

In subsequent researches it is hoped to deal with the sulphur compounds present in the 36% distillate which are not acidic but react with mercuric chloride, and also with the less volatile organic derivatives of sulphur which are present in the heavier distillates from crude Persian petroleum.

EXPERIMENTAL.

Isolation of the Organic Sulphur Compounds from " Spent Soda."— Spent soda (3 galls.), which was quite clear and apparently free from oil, was distilled during 5 hours from a 4-gallon iron drum, until oily drops could no longer be seen condensing. Great care was necessary to avoid liquid being carried over by frothing and to ensure complete condensation of the distillate, particularly at the commencement of the experiment. The yield from 40 gallons of spent soda was 720 c.c. of sulphur compounds. This material was exhaustively extracted with 50% potassium hydroxide solution, and the insoluble portion separated.

Isolation of Mercaptans.—The potassium hydroxide solution was extracted once with a small volume of ether to remove any traces of insoluble oil, diluted, and acidified with sulphuric acid, care being taken to prevent the temperature rising above 30°. The oil which separated was distilled with steam, and dried over calcium chloride, about 350 c.c. being obtained. This material was fractionally distilled, using a 24-inch Hempel column, 5°-fractions being collected. After two distillations, the curve shown in Fig. 1 was obtained,

in which, for successive fractions, the volume was plotted against the final boiling point.   Pronounced peaks occur at 57·5° and 88°, corresponding with the respective boiling points of *iso*propyl and *iso*butyl mercaptans.

After two distillations, approximately 18% of the total mixed mercaptans was obtained between 36° and 50°.   Further fractionation gave a portion, b. p. 36—38°, apparently consisting of ethyl mercaptan; the quantity was so small that further distillation was impossible.   It was therefore converted into the solid phenylcarbimide additive compound, but even from this a specimen of the

FIG. 1.   FIG. 2.

Temperature.
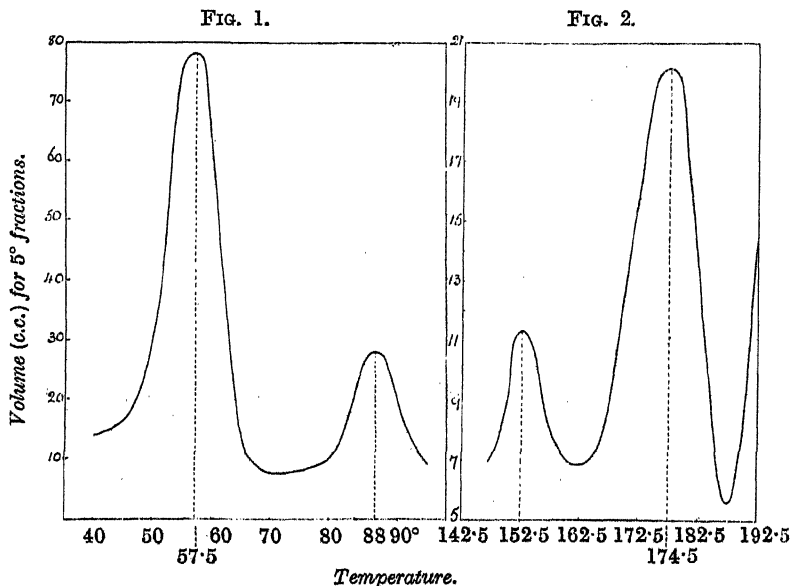
ethyl derivative free from a higher homologue could not be isolated. Nevertheless the presence of ethyl mercaptan was indicated by analysis of one of the intermediate fractions, b. p. 46—47° (Found : S, 44·8. C_3H_8S requires S, 42·1; C_2H_6S requires S, 51·6%). Moreover, the presence of ethyl mercaptan in the original spirit is quite certain, since a peak fraction consisting of diethyl disulphide was obtained during the examination of the mixed disulphides (*vide infra*).

The separation of mercaptans by distillation even of comparatively large quantities is a surprisingly difficult operation.

The fractions, b. p.'s 50—55°, 55—60°, and 60—65°, consisted almost entirely of *iso*propyl mercaptan.   After several further distillations, a fraction, b. p. 56—58°, was obtained which was

identified as *iso*propyl mercaptan (Found : S, 42·1; SH, by titration, 42·9. Calc., S, 42·1; SH, 43·4%). The crystalline derivatives were in all cases identical with those prepared from a genuine specimen of the synthetic mercaptan.

The *mercurichloride*, obtained in boiling methyl-alcoholic solution, crystallises in very insoluble plates melting above 300° (Found : Hg, 64·2, 64·6. C_3H_7ClSHg requires Hg, 64·4%).

The action of moist, freshly prepared mercuric oxide on *iso*propyl mercaptan gives the chlorine-free *derivative*, $C_3H_7 \cdot S \cdot Hg \cdot S \cdot C_3H_7$; it separates from dilute methyl alcohol in felted needles, m. p. 65° (Found : Hg, 56·9. $C_6H_{14}S_2Hg$ requires Hg, 57·1%). This compound is soluble in all the usual organic solvents. The p-*nitrobenzyl ether*, prepared from the sodium mercaptide in alcoholic solution, separates from dilute methyl alcohol in clusters of pale yellow, acicular prisms, m. p. 34° (Found : N, 6·7. $C_{10}H_{13}O_2NS$ requires N, 6·65%). The n-*propyl ether*, prepared in a similar manner, is a colourless, mobile liquid, b. p. 132°/760 mm. (Found : S, 27·2. $C_6H_{14}S$ requires S, 27·1%).

The disulphide, obtained by shaking the mercaptan with an aqueous solution of iodine, boiled at 174°; Spring and Legros (*Ber.*, 1882, **15**, 1940) give b. p. 174·5° (Found : S, 42·5. Calc., S, 42·7%). iso*Propyl phenylthiocarbamate*, $NHPh \cdot CO \cdot SPr^\beta$, was prepared by the action of an excess of the boiling mercaptan on phenylcarbimide. After spreading on porous porcelain it was crystallised from benzene–light petroleum (b. p. 40—60°), separating in clusters of long, colourless needles resembling wheatsheaves; m. p. 117—118° (Found : N, 7·4. $C_{10}H_{13}ONS$ requires N, 7·2%).*

Barium *iso*propylsulphonate : The mercaptan (6 c.c.) was added slowly and with cooling to 45 c.c. of nitric acid (d 1·3). The liquid was then warmed on the water-bath until nitrous fumes ceased to be evolved, diluted somewhat, and neutralised by means of an excess of barium carbonate. The filtered solution was mixed with sand and evaporated to dryness, and the residue, after being dried at 110°, exhaustively extracted with absolute ethyl alcohol. The soluble portion, consisting almost entirely of the barium sulphonate, was purified by dissolving in a small quantity of methyl alcohol (in which it is very soluble), adding ethyl alcohol, and boiling off the methyl alcohol. Barium *iso*propylsulphonate (Claus, *Ber.*, 1882, **5**, 660; 1875, **8**, 533) forms very small, white plates (Found : Ba, 36·0. Calc., Ba, 35·9%).

The fractions, b. p.'s 75—80°, 80—85°, and 85—90°, gave on

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* n-*Propyl phenylthiocarbamate*, long, colourless needles, m. p. 84°, and n-*butyl phenylthiocarbamate*, felted, colourless needles, m. p. 73—74°, were also prepared for purposes of comparison.

distillation a fraction, b. p. 86—88°, which was identified as *iso*butyl mercaptan (Found : S, 35·8 ; SH, by titration, 36·2. Calc., S, 35·5 ; SH, 36·7%).

The *mercurichloride*, obtained in boiling methyl-alcoholic solution, crystallises in very insoluble, infusible plates (Found : Hg, 61·7, 61·9. C_4H_9ClSHg requires Hg, 61·8%).

Di*iso*butyl disulphide, prepared by shaking the mercaptan with an aqueous solution of iodine, boiled at 215°; Spring and Legros (*loc. cit.*) give b. p. 220° (Found : S, 36·1, 35·7. Calc., S, 36·0%).

Barium *iso*butylsulphonate (Mylius, *Ber.*, 1872, 5, 978) was prepared in the manner described for the *iso*propyl derivative. It forms very small, white plates (Found : Ba, 33·4. Calc., Ba, 33·4%). iso*Butyl phenylthiocarbamate*, $NHPh \cdot CO \cdot S \cdot CH_2Pr^\beta$, prepared and purified as was the *iso*propyl ester, formed wheatsheaf clusters of long, colourless needles. The pure derivative, obtained from the synthetic mercaptan, melts at 111° (Found : N, 6·8. $C_{11}H_{15}ONS$ requires N, 6·7%). Owing to the presence of traces of the lower homologue, we were not able to obtain from our naturally occurring *iso*butyl mercaptan a sample of the phenylthiocarbamate having this melting point, our purest specimen melting at 102° (Found : N, 7·0%).

A search was made for higher mercaptans. The residue boiling above 95° gave on redistillation a fraction, b. p. 116—118°, from which the mercurichloride was prepared (Found : Hg, 60·2%). *iso*Amyl mercaptan boils at 120° [Nasini, *Ber.*, 1882, 15, 2883, gives b. p. 116·6—118° (corr.)] and its mercurichloride, $C_5H_{11}ClSHg$, requires Hg, 59·2%. Since the mercurichloride of *iso*butyl mercaptan contains 61·8% of mercury, we consider this an indication of the possible occurrence of *iso*amyl mercaptan, the most probable of the amyl mercaptans.

Isolation of Disulphides.—The portion of the mixed sulphur compounds insoluble in 50% potassium hydroxide solution was washed well with water, dried over calcium chloride, and fractionally distilled, using a 6-inch Hempel column. During the first distillation, 10°-fractions were taken, but the second time 5°-fractions were collected and the volumes of successive fractions plotted against the relevant final boiling points (Fig. 2).

The curve shows two very distinct maxima, corresponding with the boiling points of, respectively, diethyl disulphide and di*iso*propyl disulphide. Following the second peak, the curve, after falling to a minimum at about 187°, rises again, thus giving a clear indication of the presence of a higher homologue, although a third maximum was not actually obtained. An examination of the high-boiling residue has shown this higher homologue to be the di*iso*butyl com-

pound. On redistillation of the fractions of final boiling points
147·5°, 152·5°, and 157·5°, the diethyl disulphide was largely con-
centrated into the 150—182° fraction. Reduction with zinc dust
and boiling concentrated hydrochloric and glacial acetic acids,
followed by distillation in steam, gave an oil, part of which was
soluble in potassium hydroxide solution. This soluble portion was
liberated by means of dilute sulphuric acid, separated, dried over
anhydrous sodium sulphate, and distilled. The fraction boiling
below 45° was converted into the mercurichloride (Found : Hg, 67·6.
Calc. for C_2H_5ClSHg, Hg, 67·5%).

The fractions of final boiling points 172·5°, 177·5° and 182·5° were
distilled, and a fraction, b. p. 173—175°, was collected. This was
identified as di*iso*propyl disulphide by reducing it to *iso*propyl
mercaptan. The material was treated under reflux for 48 hours
with a large excess of zinc dust and boiling glacial acetic acid, the
product distilled in steam, and the volatile oil dissolved in 50%
potassium hydroxide. The alkaline solution was washed free from
unreduced disulphide with ether, acidified, and the oil which
separated washed with water, dried over calcium chloride and
distilled. The fraction, b. p. 55—60°, was identified as *iso*propyl
mercaptan by conversion into the *p*-nitrobenzyl ether, which melted
at 34° and gave no depression of melting point when mixed with a
genuine specimen.

The disulphide fraction, b. p. 210—230°, was shown to contain
di*iso*butyl disulphide by a similar procedure. The product obtained
on distillation was washed, dried, and fractionated, the portion
boiling above 80° being converted into the mercurichloride (Found :
Hg, 62·1. Calc. for C_4H_9ClSHg, Hg, 61·8%).

*The Relative Acidities of Various Mercaptans and of Hydrogen
Sulphide.*—The following series of experiments indicates quite
clearly the marked difference in the ease with which equivalent
quantities of various mercaptans and of hydrogen sulphide are
removed from solution in light petroleum by shaking with sodium
hydroxide solution.

Solutions were prepared containing approximately 1/20 gram-mol.
of the mercaptan in 250 c.c. of light petroleum (b. p. 60—80°);
two portions of 25 c.c. of each solution were then removed and
titrated iodometrically. The volumes (c.c.) of $N/10$-sodium thio-
sulphate equivalent to 25 c.c. of the light petroleum solution are
given under A below. The remaining 200 c.c. were then shaken
vigorously for 1 minute with 80 c.c. of 5% sodium hydroxide
solution (*i.e.*, about 125% excess); after allowing to settle and
removing the aqueous layer, 25 c.c. of the petroleum solution were
removed and titrated as before. The equivalent quantity (c.c.) of

sodium thiosulphate solution is given under B; the figure under C refers to the percentage decrease in the concentration of mercaptan resulting from the sodium hydroxide treatment :

Mercaptan.	$A.$	$B.$	$C = 100(A - B)/A.$
Ethyl	33·54	0·97	97·1
n-Propyl	39·23	4·38	88·8
*iso*Propyl	39·92	5·10	87·2
n-Butyl	38·67	14·23	63·2
*iso*Butyl	41·78	15·55	62·8
*iso*Amyl	42·70	28·60	33·0

Apart from the obvious decrease in the acidity of the mercaptans with increasing molecular weight, it must be noted that *n*-propyl and *n*-butyl mercaptans are slightly more acidic than their branched-chain isomerides.

Hydrogen sulphide is a much stronger acid. A solution of this substance in light petroleum, approximately $1/5N$, was completely desulphurised by shaking with 5% sodium hydroxide solution in 125% excess. An interesting confirmation of this observation was found during the isolation of the organic sulphur compounds from " spent soda," a process depending, so far as the production of mercaptans is concerned, upon the progressive hydrolysis of the sodium mercaptides present; hydrogen sulphide was not eliminated at any stage of the operation. In fact, when the very light uncondensed vapours which were evolved were passed into an alcoholic solution of mercuric chloride, the precipitated mercurichloride was quite white, and therefore free from mercuric sulphide.

CXXVII.—*The Structure of the Enolic Forms of β-Keto-esters and β-Diketones.*

By NEVIL VINCENT SIDGWICK.

IT has been shown (Sidgwick and Callow, J., 1924, **125**, 527) that in certain ortho-substituted phenols (especially the nitro- and aldehydo-compounds) a chelate ring is formed (I) in which the

I I*

hydroxyl takes part. This is proved by comparing them with their meta- and para-isomerides : the ortho-compound invariably has a lower boiling point, and is more soluble in non-polar solvents like benzene and less soluble in water, than the other two. All these properties distinguish non-hydroxylic (non-associated) substances from hydroxylic, and we can conclude that in these ortho-compounds the hydroxyl group is not free, but forms part of a ring.

The object of this paper is to show, on similar grounds, that the same structure occurs in the enolic forms of β-diketones and β-keto-esters. We cannot here compare the possibly chelate enol with an isomeric enol in which the hydroxyl group is free, but only with its isomeric ketone; and since the association or polarity of ketones is small, we should not expect, even if the enol were wholly chelate, to find so sharp a contrast as we do with the phenols. If the enol does not form a ring, it will, as a hydroxylic compound, have a higher b. p. than the ketone, and will be more soluble in hydroxylic solvents and less in hydrocarbons. If the enol is wholly chelate, it will not be associated, and its b. p. should be lower than that of the ketone, and its solubility less in water and more in non-polar solvents.

K. H. Meyer and Schöller have shown (Ber., 1920, 53, 1410) that in the absence of a catalyst acetoacetic ester can be separated to a considerable extent into its two forms by fractional distillation, and that the enol comes over mainly in the first fractions of the distillate. Thus the enol is the more volatile. In water, the solubility of the enol at 0° is 0·5%, and that of the ketone 11%—more than twenty times as great, whilst in hexane we can calculate from the equilibrium that the enol is ten times as soluble as the ketone. Hence the enol is markedly less polar than the isomeric ketone, and cannot contain a free hydroxyl group : it must be a ring compound (II).

For other keto-enols, although the volatility data are lacking, the same solubility relations can be shown to hold. The effect of the solvent on the relative solubilities of the two forms can be calculated from the proportions at equilibrium; it is not necessary to know the solubilities themselves. The van't Hoff-Dimroth

relation may be put in the form $S_e/S_k = C_e/C_k \div G$, where S_e, S_k are the solubilities of enol and ketone in the solvent used, C_e, C_k their concentrations at equilibrium, and G is a constant for the tautomeric substance, independent of the solvent. It follows that for any given tautomeric substance the ratio of the solubilities is proportional to the ratio of the concentrations at equilibrium. The measurements of K. H. Meyer (*Ber.*, 1912, **45**, 2843; 1914, **47**, 826) have shown that for 11 keto-enols (to which others were added later) including acetoacetic ester, acetylacetone, benzoyl-acetone, dibenzoylmethane, and acetyl- and benzoyl-camphor, the solubility of the enol relative to that of the ketone is always in the order water < methyl alcohol < ethyl alcohol < benzene < hexane : that is, the enol always behaves as a non-hydroxylic and non-associated substance. We may conclude that the enolic modifications of all these substances are mainly if not wholly in the chelate form.

The ring of 6 atoms with two conjugate double links which occurs in these enols as well as in the ortho-substituted phenols mentioned above, is of enormously wide distribution : it is found in the majority of mordant dyes, in derivatives of alizarin, of o-hydroxyacetophenone, of o-quinone-oximes, of nitroso-β-naphthol, of the mono- and di-oximes of α-diketones, of hydroxypyrazolones, etc. One reason for this stability may be found by calculating the strain in the ring on the simple principles of Baeyer. Of the six angles in the ring, two are between single valencies, and have the usual value of $2 \tan^{-1}\sqrt{2}$, or 109° 28'. The other four are angles between a single and a double link : this is the angle between the line joining the centre of a tetrahedron to one apex and that joining it to the middle point of an opposite edge : the value of this is $180° - \tan^{-1}\sqrt{2}$. Thus the sum of the six angles of the ring in an unstrained condition is $4(180° - \tan^{-1}\sqrt{2}) + 2 \times 2 \tan^{-1}\sqrt{2} = 720°$, the exact sum of the angles of a plane hexagon. In other words, this form of ring * is entirely without strain. This conclusion is, of course, subject to the validity of certain simplifying assumptions; but it may be taken to be an approximation to the truth, and to afford an explanation of the remarkable stability of this type of ring.

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OXFORD. [*Received, March 19th*, 1925.]

* The same remarks apply to the quinone ring.

NOTES.

Ray's Supposed Triethylene Trisulphide. By GEORGE MACDONALD
BENNETT and WILLIAM AMBLER BERRY.

MORE than two years ago one of us made the suggestion (J., 1922,
121, 2144, footnote) that the substance described by Râly (J.,
1920, **117**, 1090) as triethylene trisulphide was probably identical
with the well-known diethylene disulphide (1 : 4-dithian). As
this suggestion was not accepted (J., 1923, **123**, 2178, footnote),
and as further reactions of " triethylene trisulphide " have been
described (*J. Indian Chem. Soc.*, 1924, **1**, 63), the question has now
been tested by direct experiment. The preparation was repeated
as described by Râly, and 1·2 g. of the crystalline substance were
obtained, of m. p. 113° (corr.) (Found : C, 39·9 ; H, 6·5. Calc.,
C, 40·0 ; H, 6·7%). The molecular weight of the substance in
nitrobenzene solution agrees with the formula $C_4H_8S_2$ (Found :
M, 128, 126. Calc., *M*, 120).* The substance was compared
directly with a specimen of dithian prepared as described by V.
Meyer (*Ber.*, 1886, **19**, 3260) : this melted at 113°, and its mixture
with the supposed triethylene trisulphide melted equally sharply
at the same temperature. The two substances had the same
characteristic odour, the same remarkable volatility at laboratory
temperature, and the same boiling point (200°). Their identity
was finally confirmed by examination under the microscope, the
crystals being clearly identical both in form and in optical properties.

It is unnecessary to discuss in detail the reactions which have
been attributed to this " triethylene trisulphide," but it may be
mentioned that among the substances prepared from it the " tri-
sulphone " (J., 1923, **123**, 2174) was evidently identical with Bau-
mann and Walter's disulphone (*Ber.*, 1893, **26**, 1132), and the
" disulphone " was presumably an impure specimen of the same
substance, and that the case of a nine-membered ring compound
yielding a six-membered ring compound under the influence of ethyl
iodide in alcoholic solution (J., 1922, **121**, 1279) no longer requires
any explanation.

It is evident that in some cases the derivatives described were
not homogeneous substances, and this appears all the more probable
where they were not purified by recrystallisation. The substance
formulated as $(C_2H_4)_3S_3PtCl_4$, for instance (*loc. cit.*, p. 1283), was
taken from a succession of crops of material giving analytical
figures agreeing approximately with the formula stated. It is

* Sir P. C. Râly is mistaken in supposing that a molecular-weight deter-
mination had previously been made by us with the substance ; this method
of testing the formula was left open to him in the first instance.

now doubtful whether this crop was more homogeneous than those that preceded it.

Our thanks are due to the Department of Scientific and Industrial Research for a grant which has enabled one of us (W. A. B.) to take part in this work.—UNIVERSITY OF SHEFFIELD. [*Received*, *March 6th*, 1925.]

The Physiological Action of certain Benzothiazoles and Mercaptan Derivatives. By ROBERT FERGUS HUNTER.

4'-AMINO-1-PHENYL-5-METHYLBENZOTHIAZOLE (*J. Soc. Chem. Ind.*, 1923, **42**, 302) and certain related compounds have been found to have a peculiar action on the skin of the face and hands.

Hot solutions of dehydrothiotoluidine in contact with the skin develop an unpleasant form of eczema. The effect is worst between the fingers, and the irritation is intense during the first few days. The skin rises in peculiar, practically colourless blisters, which break, liberating a colourless infectious liquid which spreads the trouble.

Observations of this nature have been made by other investigators with regard to related sulphur compounds. Thus Hofmann (*Ber.*, 1887, **20**, 2251) states that the vapour of *o*-aminophenyl mercaptan has a most detrimental effect on the skin, producing intense irritation and swelling. The author has observed a similar effect produced by the higher homologue of this compound, namely, the thiocresol which results on the alkali fusion of dehydrothiotoluidine.

Bathing the infected skin in hot water relieves the irritation to a certain extent, and treatment with 2% aqueous phenol also has a beneficial action.—THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W. 7. [*Received, February 28th,* 1925.]

Preparation of 1-p-*Sulphophenyl*-3-*methyl*-5-*pyrazolone.* By GEORGE REEVES.

INGOLD (*J.*, 1921, **119**, 329) has put forward evidence in favour of the view that in condensations between tautomeric substances of the keto-enol type and substances which have active hydrogen the tautomeric substance reacts in the enolic form, the unsaturated linking being responsible for the initial condensation and the elimination of water being a subsequent effect. The methods employed to effect condensation between ethyl acetoacetate and phenylhydrazine-*p*-sulphonic acid (Cain, " Manufacture of Intermediate Products for Dyes," 1918 edition, p. 162; Fierz-David, " Grundlegende Operationen der Farbenchemie," 1924 edition, p.

144) do not favour preliminary enolisation of the ester, which is apparently considered to react in the keto-form, and it occurred to the author to attempt the preparation of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone under conditions which would tend to the preliminary enolisation of the ester, this being accomplished by using sodium phenylhydrazine-*p*-sulphonate in somewhat alkaline solution.

A solution of sodium phenylhydrazine-*p*-sulphonate (from 94 g. of the acid) in 750 c.c. of water was made strongly alkaline to litmus and treated quickly at 28° with 65 g. of redistilled ethyl acetoacetate. This dissolved at once and the temperature rose to 36°. After 15 minutes, the solution was heated at 90° for 2 hours, and then acidified with 100 c.c. of hydrochloric acid (28%), a copious precipitate forming rapidly. After 12 hours, the crystalline cake was collected and washed very quickly with a little water. The moist product weighed 226 g. and contained 123 g. of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone (analysis by titration with $N/10$-benzenediazonium chloride). It was very clean and quite pure enough for use as an intermediate for dyes.—THE ORCHARD, CHADDESDEN, DERBY. [*Received, February 11th, 1925.*]

The Micro-estimation of Methoxyl. By JOHN CHARLES SMITH.

IN using the method of Pregl (micro-Zeisel) for the estimation of methoxyl, very low results were obtained until it was noticed that the filtrate from the silver iodide gave a further precipitate on dilution with large quantities of alcohol and water. The silver nitrate stock solution had been made by dissolving 20 g. of silver nitrate in 200 g. of 95% alcohol as recommended in the English translation of Pregl's " Die Quantitative Organische Mikroanalyse " (Springer, Berlin, 1923). Reference to the German edition, however, showed that the concentration of the solution should be 20 g. of silver nitrate in 500 g. of 95% alcohol, and this was found to give good results.

The analyses were carried out on a very pure specimen of quinol monomethyl ether, m. p. 56° (OMe, 25·0%).

a. AgNO₃ soln., 20 g. in 200 g. of 95% EtOH.			*b.* AgNO₃ soln., 20 g. in 500 g. of 95% EtOH.		
Mg. of subs.	Mg. of AgI.	OMe %.	Mg. of subs.	Mg. of AgI.	OMe %.
3·263	5·504	22·3	3·335	6·178	24·5
3·841	4·500	15·5	3·828	7·218	24·9
3·110	4·431	18·8	4·396	8·304	24·9

THE UNIVERSITY, MANCHESTER.   [*Received, March 20th, 1925.*]

Second Report of the International Committee of the International Union of Pure and Applied Chemistry on the Chemical Elements.

INTERNATIONAL ATOMIC WEIGHTS, 1925.

EXPLANATION OF THE TABLE.

IN this table, the primary standard is, as usual, O = 16·000. We have retained the old value for the secondary standard, Ag = 107·880, although we are of the opinion that this value is slightly higher than the true one. If a more probable value (between 107·870 and 107·876) had been adopted for this secondary standard, many atomic weights dependent upon it (about 42 in number) would be lowered in the same proportion. Since the difference is of slight importance for most purposes, we believe it advisable to avoid the inconvenience of a change until more certain evidence has been obtained. The new table, which is arranged according to the alphabetical order of the International symbols of the elements * (second column), differs in several points from the table published by the former Committee.

First : The third column contains the atomic (or Moseley) numbers of the elements in italics.

Secondly : The atomic weights are given with one uncertain decimal place (except in the case of hydrogen—see below). This is in accord with usual scientific practice. Those persons who prefer fewer decimal places may easily round off the values to suit their needs. For analytical commercial purposes the use of the complete values given in the table is recommended in order to avoid conflicting reports from different analysts.

In accordance with the application of this principle the atomic weights of the following 23 elements have been slightly changed by being expressed with one more decimal place than in the previous table. The values of the fundamental atomic weights given in the table have been used in computing the others.

Ag—Ar—Br—Cl—Cr—Dy—F—Gd—Hg—I—K—Li—Na—Nd—O—P—Pr—Pt—Ra—Rh—S—U—V.

On the other hand, the second decimal has been omitted in the case of krypton; and all decimal places have been omitted in the case of zirconium (for the zirconium material examined up to the present time has undoubtedly been a mixture of two elements), to which the round number 91 is given.

Thirdly : In divers new investigations the atomic weights of 24 elements have been revised. The changes which seem to us

* [In accordance with the usage of the Journal, the elements are given in the table in the alphabetical order of their names.—EDITOR.]

desirable in the light of the new work are included in the table. The following elements are those affected : Al—B—Be—Ga—Ge—La—Sb—Sc—Si—Sm—Sn—Tl.

A brief summary of the results of these recent investigations is appended so that those who wish to verify the conclusions may easily consult the original records.

Furthermore, since an additional decimal place has been added in the case of most of the fundamental atomic weights, more detailed evidence upon which these changes are bases is cited in conformity with the procedure adopted regarding the other changes made in the old International Table.

Aluminium.—RICHARDS and KREPELKA (*J. Amer. Chem. Soc.,* 1920, **42**, 2221) find Al = 26·96 from the ratio AlBr$_3$: 3Ag.

Recently (in a paper communicated to the *Bohemian Academy* and to the *J. Amer. Chem. Soc.*) KREPELKA finds from the ratio AlCl$_3$: 3Ag, as a mean of 11 very concordant experiments, Al = 26·972, a value slightly higher (by 0·009) than that obtained from the bromide.

Antimony.—Sb = 121·77. WILLARD and McALPINE (*J. Amer. Chem. Soc.,* 1921, **43**, 797) have determined the ratio SbBr$_3$: 3Ag and SbBr$_3$: 3AgBr.

Beryllium.—HÖNIGSCHMID and BIRCKENBACH (*Ber.,* 1922, **55**, 4) find from the ratios BeCl$_2$: 2Ag and BeCl$_2$: 2AgCl the value Be = 9·018.

Boron.—BAXTER and SCOTT (*Science N. S.,* 1921, **54**, 524) reported the preliminary value B = 10·83. HÖNIGSCHMID and BIRCKENBACH (*Anal. Fis. Quím.,* 1922, **20**, 167) find from the ratio BCl$_3$: 3Ag, B = 10·817—10·838, and from the ratio BCl$_3$: 3AgCl, B = 10·818—10·842. The authors prefer B = 10·82. Recently BAXTER and SCOTT (*Proc. Amer. Acad.,* 1923, **59**, 21) find from the ratio BCl$_3$: 3Ag, B = 10·820 as a mean of 22 experiments; from the ratio BCl$_3$: 3AgCl (7 experiments), B = 10·824; from the ratio BBr$_3$: 3Ag (14 experiments), B = 10·822; from the ratio BBr$_3$: 3AgBr (2 experiments), B = 10·812. The mean of all analyses is B = 10·820.

Bismuth.—HÖNIGSCHMID and BIRCKENBACH (*Ber.,* 1921, **54**, 1873) find Bi = 209·00 from the ratios BiCl$_3$: 3Ag and BiBr$_3$: 3Ag.

Bromine.—Br = 79·916. Ag : AgBr = 0·574453; AgBr : AgCl = 1·310171. BAXTER (*Proc. Amer. Acad.,* 1906, **42**, 202). Br : Ag = 0·740786; Br : AgBr = 0·425547. HÖNIGSCHMID and ZINTII (*Annalen,* 1923, **433**, 201).

Carbon.—C = 12·000. CO$_2$: C = 2·6660 (Clarke, " A Recalculation of the Atomic Weights," 4th Ed., *Memoir of the Nat. Acad. Science,* vol. XVI, No. 3).

Chlorine.—Cl = 35·457. AgCl : Ag = 1·32867. RICHARDS and WELLS (*Pub. Carn. Inst.,* No. 28, 1905) AgBr : AgCl = 1·310171. BAXTER (*Proc. Amer. Acad.,* 1906, **42**, 202).

Chromium.—BAXTER, MUELLER, and HINES (*J. Amer. Chem. Soc.*, 1909, **31**, 329) $Ag_2CrO_4 : 2Ag$; BAXTER and JESSE (*ibid.*, 1909, **31**, 541) $Ag_2Cr_2O_7 : 2Ag$, find $Cr = 52 \cdot 01$.

Cobalt.—$Co = 58 \cdot 94$. BAXTER and DORCAS (*J. Amer. Chem. Soc.*, 1924, **46**, 357) find from the analysis of the chloride that both terrestrial and meteoric cobalt possess the atomic weight $58 \cdot 94$.

Fluorine.—SMITH and VAN HAAGEN (*Pub. Carn. Inst.*, No. 267, 1918) find $F = 19 \cdot 00$.

Gallium.—RICHARDS with W. M. CRAIG (*Bull. Soc. chim.*, 1922, **31**, 929) from the ratio $GaCl_3 : 3Ag$ find $Ga = 69 \cdot 716$; see also *J. Amer. Chem. Soc.*, 1923, **45**, 1155.

Germanium.—$Ge = 72 \cdot 60$. BAXTER and COOPER (*Proc. Amer. Acad. Arts and Sciences*, 1924, **59**, 235) find from the ratio $GeCl_4 : 4Ag$ the atomic weight $Ge = 72 \cdot 60$. They have confirmed the result by the analysis of the bromide (not yet published).

Holmium.—$Ho = 163 \cdot 4$. HOLMBERG (*Z. anorg. Chem.*, 1911, **71**, 226).

Hydrogen.—The best gravimetric and gasometric determinations give for the atomic weight of this element values lying between $1 \cdot 0075$ and $1 \cdot 0078$. The rounded value $1 \cdot 008$ suffices for all practical purposes.

Iodine.—$I = 126 \cdot 932$. $Ag : I = 0 \cdot 849906$. BAXTER (*J. Amer. Chem. Soc.*, 1910, **32**, 1591).

Lanthanum.—$La = 138 \cdot 90$. BAXTER, TANI, and CHAPIN (*J. Amer. Chem. Soc.*, 1921, **43**, 1080) find $La = 138 \cdot 91$. HOPKINS and DRIGGS (*ibid.*, 1922, **44**, 1927) find $La = 138 \cdot 89$.

Lithium.—$Li = 6 \cdot 940$. $LiCl : AgCl = 0 \cdot 29579$; $LiCl : Ag = 0 \cdot 39299$. RICHARDS and WILLARD (*Pub. Carn. Inst.*, 1910, No. 25, 1).

Mercury.—$Hg = 200 \cdot 61$. EASLEY, then BAKER and WATSON (see Clarke's "Recalculation of the Atomic Weights," 4th Ed., 1920, pp. 200—205). HÖNIGSCHMID, BIRCKENBACH, and STEINHEIL (*Ber.*, 1923, **56**, 1212).

Neodymium.—$Nd = 144 \cdot 27$. BAXTER and CHAPIN (*J. Amer. Chem. Soc.*, 1911, **33**, 1). BAXTER, WHITCOMB, and STEWART (*ibid.*, 1916, **38**, 302).

Phosphorus.—$P = 31 \cdot 027$. $3AgBr : Ag_3PO_4 = 1 \cdot 34562$. BAXTER and JONES (*Proc. Amer. Acad.*, 1910, **45**, 137); $PBr_3 : 3Ag = 0 \cdot 836647$; $PBr_3 : 3AgBr = 0 \cdot 480623$. BAXTER, MOORE, and BOYLSTON (*ibid.*, 1912, **47**, 585); $PCl_3 : 3AgCl = 0 \cdot 319509$; $PCl_3 : 3Ag = 0 \cdot 424507$. BAXTER and MOORE (*J. Amer. Chem. Soc.*, 1912, **34**, 1644).

Platinum.—$Pt = 195 \cdot 23$. ARCHIBALD (*Proc. Roy. Soc. Edin.*, 1909, **29**, 721).

Potassium.—$K = 39 \cdot 096$. $KCl : AgCl = 0 \cdot 52012$; $KCl : Ag = 0 \cdot 69107$. RICHARDS and MUELLER (*Pub. Carn. Inst.*, 1907, No. 69, 27).

Praseodymium.—Pr = 140·92.   BAXTER and STEWART (*J. Amer. Chem. Soc.*, 1915, **37**, 516).

Radium.—Ra = 225·95.   HÖNIGSCHMID (*Monatsh.*, 1911, **33**, 253; *Wien. Akad.*, Nov. 1912, 121).

Radon.—Formerly *Niton.*   The round number Rn = 222 appears the most probable from radioactive evidence.

Samarium.—Sm = 150·43.   STEWART and JAMES (*J. Amer. Chem. Soc.*, 1917, **39**, 2605).   OWENS, BALKE, and KREMERS (*ibid.*, 1920, **42**, 515).

Scandium.—Sc = 45·10.   HÖNIGSCHMID (*Z. Elektrochem.*, 1919, **25**, 93).

Silicon.—Si = 28·06.   BAXTER, WEATHERILL, and SCRIPTURE (*Proc. Amer. Acad.*, 1923, **58**, 245) find from the ratio $SiCl_4 : 4Ag$, Si = 28·063; from $SiBr_4 : 4Ag$, Si = 28·059.   Mean of the best series : Si = 28·061.

Sulphur.—S = 32·064. $2AgCl : Ag_2SO_4 = 0·91933$.   RICHARDS and JONES (*Pub. Carn. Inst.*, 1907, No. 69, 69); $Na_2SO_4 : Na_2CO_3 = 1·34016$; $Na_2CO_3 : 2Ag = 0·491265$.   RICHARDS and HOOVER (*J. Amer. Chem. Soc.*, 1915, **37**, 95).

Thallium.—Tl = 204·39.   HÖNIGSCHMID, BIRCKENBACH, and KOTHE (*Sitzungsber. Bayer. Akad. Wiss.*, 1922, 179) find from the ratio TlCl : Ag, Tl = 204·39; and from the ratio TlCl : AgCl, Tl = 204·39.

Thulium.—Tm = 169·4.   JAMES and STEWART (*J. Amer. Chem. Soc.*, 1920, **42**, 2022) find Tm = 169·39.

Titanium.—BAXTER and FERTIG (*J. Amer. Chem. Soc.*, 1923, **45**, 1228) find by analysis of the tetrachloride, Ti = 47·85.   Since this result is preliminary, no change is recommended.

Yttrium.—Y = 88·9.   Mean of the best determinations.

Zinc.—Zn = 65·38.   RICHARDS and ROGERS find Zn = 65·376 (*Proc. Amer. Acad.*, 1895, **31**, 158); BAXTER and GROSE find Zn = 65·389 (*J. Amer. Chem. Soc.*, 1916, **38**, 868); BAXTER and HODGES find Zn = 65·381 (*ibid.*, 1921, **43**, 1242).

F. W. ASTON.
GREGORY P. BAXTER.
BOHUSLAV BRAUNER.
A. DEBIERNE.
A. LEDUC.
T. W. RICHARDS.
FREDERICK SODDY.
G. URBAIN.

[Celtium / Hafnium] HÖNIGSCHMID and ZINTL (*Ber.*, 1925, **58**, 453) determined the ratio of the tetrabromide to AgBr with two samples found by THAL JANTZEN (by *X*-ray analysis) to contain (I) 0·57, (II) 0·16% Zr.   From I they find the atomic weight of the element to be 178·64 ± 0·09 : from II, 178·57 ± 0·03.   As the most probable value they give 178·6 ± 0·05.—EDITOR.]

International Table of Atomic Weights of the Chemical Elements. 1925.

	Symbol.	At. No.	At. weight.		Symbol.	At. No.	At. weight.
Aluminium ...	Al	13	26·97	Mercury	Hg	80	200·61
Antimony	Sb	51	121·77	Molybdenum	Mo	42	96·0
Argon	A (Ar)	18	39·91	Neodymium ...	Nd	60	144·27
Arsenic	As	33	74·96	Neon	Ne	10	20·2
Barium	Ba	56	137·37	Nickel	Ni	28	58·69
Beryllium	Be }	4	9·02	Nitrogen.........	N	7	14·008
Glucinium	Gl }			Osmium	Os	76	190·8
Bismuth	Bi	83	209·00	Oxygen	O	8	16·000
Boron	B	5	10·82	Palladium	Pd	46	106·7
Bromine	Br	35	79·916	Phosphorus ...	P	15	31·027
Cadmium	Cd	48	112·41	Platinum	Pt	78	195·23
Caesium	Cs	55	132·81	Potassium	K	19	39·096
Calcium	Ca	20	40·07	Praseodymium	Pr	59	140·92
Carbon	C	6	12·000	Radium	Ra	88	225·95
Cerium	Ce	58	140·25	Radon	Rn	86	222
Chlorine	Cl	17	35·457	Rhodium	Rh	45	102·91
Chromium	Cr	24	52·01	Rubidium	Rb	37	85·44
Cobalt............	Co	27	58·94	Ruthenium ...	Ru	44	101·7
Columbium ...	Cb }	41	93·1	Samarium	Sm	62	150·43
Niobium	Nb }			Scandium	Sc	21	45·10
Copper	Cu	29	63·57	Selenium	Se	34	79·2
Dysprosium ...	Dy	66	162·52	Silicon	Si	14	28·06
Erbium	Er	68	167·7	Silver	Ag	47	107·880
Europium	Eu	63	152·0	Sodium	Na	11	22·997
Fluorine	F	9	19·00	Strontium	Sr	38	87·63
Gadolinium ...	Gd	64	157·26	Sulphur	S	16	32·064
Gallium	Ga	31	69·72	Tantalum	Ta	73	181·5
Germanium ...	Ge	32	72·60	Tellurium	Te	52	127·5
Gold	Au	79	197·2	Terbium	Tb	65	159·2
Helium	He	2	4·00	Thallium	Tl	81	204·39
Holmium	Ho	67	163·4	Thorium	Th	90	232·15
Hydrogen	H	1	1·008	Thulium	Tm	69	169·4
Indium	In	49	114·8	Tin	Sn	50	118·70
Iodine	I (J)	53	126·932	Titanium	Ti	22	48·1
Iridium	Ir	77	193·1	Tungsten ...... }	W	76	184·0
Iron	Fe	26	55·84	Wolfram.......... }			
Krypton	Kr	36	82·9	Uranium	U	92	238·17
Lanthanum ...	La	57	138·90	Vanadium	V	23	50·96
Lead	Pb	82	207·20	Xenon	Xe	54	130·2
Lithium	Li	3	6·940	Ytterbium	Yb	70	173·6
Lutecium	Lu	71	175·0	Yttrium	Y	39	88·9
Magnesium ...	Mg	12	24·32	Zinc	Zn	30	65·38
Manganese ...	Mn	25	54·93	Zirconium	Zr	40	91

[Celtium }At. number 72. At. weight 178·6.—EDITOR.]
[Hafnium }

ANNUAL GENERAL MEETING,

PROFESSOR W. P. WYNNE, D.Sc., F.R.S., the President, occupied the Chair.

The TREASURER made a statement concerning the finances of the Society for 1924, and the Report of Council, together with the Balance Sheets and Statements of Accounts for the year ending 31st December, 1924, was adopted on the proposal of Professor H. E. ARMSTRONG, seconded by Professor G. G. HENDERSON.

REPORT OF COUNCIL, 1924–1925.

I. *Fellowship Statistics.*

THE number of Fellows at 31st December, 1923, was 3978. During the year, 257 Fellows were elected and 8 reinstated, making the gross total 4243. The number of deaths recorded during the period under review was 45; the resignations numbered 121, as against 86 the previous year, while the names of 107 Fellows have been removed for non-payment of annual subscription, and election in the case of 7 new Fellows has been declared void. The number of Fellows at the 31st December, 1924, was, therefore, 3963, and is less by 15 than at the end of 1923.

Among the Fellows whose deaths have been recorded during the year 1924 are Sir James Dobbie, who held the office of President from 1919—1921 and served on the Council for 12 years in all; Professor G. D. Liveing, who was a Vice-President for 7 years and who celebrated in 1923 his 70 years of Fellowship; Sir George Beilby, who was a Vice-President for 3 years and an Ordinary Member of Council for 4 years; and Mr. Otto Hehner, who served on the Council for 4 years. Obituary notices of Sir James Dobbie and Mr. Otto Hehner, prepared by Prof. W. N. Haworth and Dr. B. Dyer, respectively, appeared in the Journal for December.

The congratulations of the Society have been conveyed to Mr. George W. Knox (elected June 16th, 1864) and Mr. Thomas P. Blunt (elected February 2nd, 1865), who have completed 60 years of Fellowship, and to the following, who, during the year, have completed their jubilee as Fellows :

	Elected.
Alfred John Greenaway	April 2nd, 1874.
Frederick William Fletcher	April 16th, 1874.
Harcourt Henry Benjamin Shepherd	May 21st, 1874.
George Christopher	June 18th, 1874.
James Alfred Kendall	Dec. 17th, 1874.
John William Biggart	Feb. 18th, 1875.
Joseph John Acworth	March 4th, 1875.
Joseph Gordon Gordon	March 4th, 1875.

II. *Changes in Officers.*

The Council accepted with much regret in April last the resignation of Prof. Irvine Masson from the office of Secretary on his appointment to a Chair of Chemistry in the University of Durham, and desires to record its appreciation of the ability and zeal with which he conducted the Society's affairs during the two and a half years he filled this position. Dr. T. Slater Price was appointed Secretary until the Annual General Meeting in 1925 to fill the vacancy thus caused.

The Council also accepted with much regret the resignation from the Chairmanship of the Library Committee of Professor J. M. Thomson, whose services in directing the policy of that Committee during a period of twenty years have been invaluable and to whose efforts the comprehensive character of the Library is largely due. Nor should it be forgotten that the Chairmanship, from which he has resigned, is only one of many offices which Professor Thomson has filled to the great advantage of the Society during a period extending over forty-five years. In succession to Professor Thomson Professor J. R. Partington was appointed Chairman of the Library Committee.

III. *Publications.*

The Journal for 1924 contains 2698 pages, of which 2605 pages are occupied by 363 memoirs and 31 notes, the remaining 93 pages being devoted to Obituary Notices, the Hugo Müller and Faraday Lectures, the Report of the General Meeting, and the Presidential Address. The volume of the preceding year contained 400 memoirs and 11 notes, occupying 3258 pages. The activity in British chemical research reflected in the size of the Journal for 1923 was therefore well maintained during 1924. Early in the year, instructions were received from the Council, that, owing to financial stringency, authors should be requested to write their papers as concisely as possible and thus reduce the cost of publication. With this end in view, a new system of refereeing papers was instituted, whereby every paper received by the Society was to be sent to two referees, one of whom must be a member of the Publication Committee. The latter provision necessitated an enlargement of the Committee in order that there should be no delay in the consideration of papers : seven new members were therefore added to that body, increasing its membership to 26. In October the Council deemed it desirable that the Publication Committee should have its own Chairman, and appointed Dr. N. V. Sidgwick to the office.

The transition from the old to the new system involved considerable delay in the publication of papers; this delay was at its

worst in June, when no fewer than 91 papers were in the hands of referees or authors. The congestion was gradually relieved during the succeeding months, and by the end of the year the position was normal, the number of papers under consideration being 20 only.

The appointment of a full-time Editor for the Journal has in the opinion of the Council justified itself, but bearing in mind the possibilities of accident or illness, the work of the Journal cannot be regarded as satisfactorily provided for until he has the assistance of a Sub-editor. How closely he is tied to the work of the Journal will be evident from the fact that to allow him some holiday during last summer, the President undertook to see the August number of the Journal through the press.

The "Abstracts of Chemical Papers" (A. Pure Chemistry) has been issued as a separate publication for which the Bureau of Chemical Abstracts is responsible (v. Report of Council, J.C.S., 125, 1924, p. 969). Part I, covering Organic Chemistry and Biochemistry, contained 1396 pages. Part II, covering General and Physical Chemistry, Inorganic Chemistry, Mineralogical Chemistry, and Analytical Chemistry, contained 876 pages.

IV. *Library.*

There is ample evidence of the increasing usefulness of the Library. During 1924 there were 6652 attendances, as against 6403 in 1923, 4486 of these being made by Fellows of the Chemical Society and 2166 by members of contributing Societies; the number of books borrowed was 4509, compared with 4136 the previous year. The additions to the Library comprise 289 books, of which 101 were presented, 560 volumes of periodicals, and 164 pamphlets, the corresponding figures for last year being 343, 494, and 110, respectively. The Library now contains 28,424 volumes, consisting of 8661 books and 19,763 bound volumes of periodicals.

Despite the yearly increase in the number of books and in the number of those who use the Library, the space available for reading has still to be restricted to one room encumbered with stacks of bookshelves, causing inconvenience and discomfort to all concerned. While the urgency of the need for additional accommodation for all purposes, and particularly for the Library, continues to engage the attention of the Council, active steps to meet it seem to be precluded by the present financial stringency.

During 1924, £1769 4s. 10d. was spent on the Library, and towards this sum £636 15s. was contributed by kindred societies. In this connexion, the Council acknowledges its indebtedness to the Institute of Chemistry, which has increased its subscription from

£100 to £250, and to the Research Association of British 'Rubber and Tyre Manufacturers for a special contribution of £10 10s. The Council is also glad to record that the Institute of Brewing now contributes to the expenses of the Library, and desires again to acknowledge that without the substantial help of the contributing societies the advantages afforded by the joint Library scheme could not be adequately maintained.

V. *General.*

The Faraday Lecture entitled " Atomism in Modern Physics " was delivered by Professor R. A. Millikan in the Theatre of the Royal Institution on June 12th, 1924, and the special lecture on " Problems presented by Films on Solid Surfaces " was given by Sir William Hardy on February 26th, 1925, in the Lecture Hall of the Institution of Mechanical Engineers. The continued large attendance at these special lectures, the first series of which was instituted in 1915, affords evidence that their interest and appeal is not exhausted, and, on behalf of the Society, the Council desires to express its great indebtedness to those who deliver them.

The mutual arrangement reached last year between the American Chemical Society, the Society of Chemical Industry, and the Chemical Society, whereby the members of any one of these Societies may obtain the publications of the other two on privileged terms, has been continued.

It has also been arranged to exchange 20 sets of the " Journal of the Chemical Society " from 1915 to 1924 for a like number of sets of the Berichte for the same period. These sets are now obtainable from the Assistant Secretary at £22 each, plus cost of carriage.

The Society was represented by the President at the celebrations of the coming of age of the University of Leeds and jubilee of its parent foundation the Yorkshire College; by Professor F. G. Donnan at the centenary celebrations of the Franklin Institute; by Professor J. C. Philip at the Kelvin centenary celebrations; by Professor T. M. Lowry at the banquet given by the Société Chimique de France; by Professor J. F. Thorpe at the centenary celebrations of the Rensselaer Polytechnic Institute held at Troy, U.S.A. In connexion with the 50th anniversary of the foundation of stereo-chemistry by van't Hoff and Le Bel, in 1874, the Society was represented by Professor H. E. Armstrong, and by Professor T. M. Lowry at the celebrations held by the Dutch Chemical Society in Amsterdam, and by Sir William Pope at the celebrations organised by the French Chemical Society in Paris.

In response to an invitation from the Royal Institution, the Council appointed Sir William Pope its representative on the

committee formed to organise the celebration of the discovery of benzene by Faraday at the Royal Institution (June 16th, 1825).

Sir William Tilden has been reappointed to represent the Society on the Court of Bristol University; Professor C. S. Gibson, Sir William Pope, and Professor J. F. Thorpe have been appointed to represent the Chemical Society on the Federal Council for 1924; and Professor Lowry was reappointed for a further two years on the Editorial Board of the Journal of Physical Chemistry.

The Congratulations of the Society on the formation of the Indian Chemical Society were conveyed to Sir Prafulla C. Rây, the first President.

The Council has made a contribution of £100 towards the cost of publishing the " Annual Tables of Constants."

The Council has had under consideration the question whether the titles of papers which have been received by the Society should continue to be published in the Proceedings. As in its opinion such publication serves a useful purpose in making known the fact that investigations covered by the titles have reached the stage at which the results of work in progress can be communicated, and as it may avoid overlapping, it has been decided to continue the practice.

The appreciative thanks of the Council have been accorded to General J. B. Dumas for a typescript of the Life of J. B. Dumas, and to Professor P. P. Bedson for a medal of G. Lunge struck in honour of his 70th birthday.

The Harrison Memorial Prize Selection Committee has met during the past year. As reported to the Council, the Committee came to the conclusion that none of the candidates making application complied with the conditions set out in Clause 9 of the Trust Deed and it was again unable to recommend an award of the Prize. Negotiations with the donors of the Harrison Memorial Prize Fund have been initiated with the object of securing, if possible, a modification of the terms of this clause.

The Council desires to record its indebtedness to those Fellows who have contributed to the Annual Reports for 1924.

The present representatives of the Chemical Society on the Bureau of Chemical Abstracts are Professor C. S. Gibson, Professor G. T. Morgan, Professor J. F. Thorpe, and Professor W. P. Wynne. During the past year, as reported to the Council, the Bureau approached the American Chemical Society with regard to the possibility of organising a single publication in the English language of Abstracts of chemical papers; but the correspondence made it clear that opinion on the other side is definitely against such a scheme. In these circumstances the Bureau has devoted itself to developing plans for the unification of British Abstracts; proposals

have been put forward with this end in view and discussed by the Council, which still has the matter under consideration.

VI. *Financial.*

The Finance Committee met on four occasions during the year. Its membership was enlarged from nine to eleven last April, and in May the Treasurer was appointed Chairman of the Committee by the Council.

Last year the Society was faced with an adverse balance of £1628 15s. 9d., and, in his report to the Council, the Treasurer pointed out that if the same rate of expenditure were maintained, and no new sources of income were created, the adverse balance for the year 1924 would be between £2000 and £3000. The outlook was serious, because the Society had already been committed to a considerable increase in the amount of editorial salaries consequent on the retirement of Mr. Greenaway, the appointment of a full-time Editor of the Journal, and the establishment of the Bureau of Abstracts.

The Council had, therefore, to consider the best means of reducing the expenditure and increasing the income of the Society, for it was evident that the financial position could only be readjusted by the institution of a period of drastic economy, after which it would be clear how the Society stood as regards the amount of expenditure it could carry with the income available.

After carefully considering various ways and means of securing this object, the Council decided to increase the price to the public of the Journal and Abstracts and of the Annual Reports, to omit printing the List of Fellows for 1924, and to make a charge of 5s. 6d. to Fellows for the Annual Reports.

The full effect of some of these changes will not be felt until next year, but their influence on the balance sheet of the present annual period has already been considerable. The List of Fellows was not published and this resulted in a saving of £110 4s. 9d.; further, there were increases in the receipts from the sale of (a) the Annual Reports (£250 19s. 2d.), and (b) the Journal and Abstracts (£364 15s. 6d.).

The Council had also under consideration the question of reducing the large sum of £474 15s. 6d. which appears in the accounts for 1923 under the item " Authors' Copies," and at an Extraordinary General Meeting on June 26th power was given to the Council to charge authors the cost price of reprints of their papers appearing in the Journal. Before arrangements had been completed to give effect to this change in the Bye-Law, the position had so changed that it was possible for the Council to continue the issue of reprints gratis in a modified form, each author, or part

author, of a paper in the Journal now receiving 10 copies of the paper free of charge.   These reprints are supplied without wrappers, but each reprint bears the volume, number, and year of the Journal, and any author can obtain additional copies of his reprints in wrappers by paying the extra cost.   The effect of this economy will not be evident until the accounts for the year 1925 are published, but it is estimated that the cost to the Society of authors' copies will be reduced by about one-half.

Nevertheless, in spite of the effect these minor economies would have on the general financial position, it was clear to the Council that they would be insufficient to meet the situation unless the chief expenditure the Society incurs, namely that due to its publications, could be substantially reduced.   The chief publications of the Society are the Journal and Abstracts, the cost of which in 1923 represented 65 per cent. of the total expenditure incurred. It was evident that it would be difficult to effect any considerable reduction in the cost of the Abstracts, the volume of which is determined by many conditions over which the Council has no control, and it followed, therefore, that the main burden of retrenchment would have to fall upon the Journal.

Bearing in mind the chief object for which the Society exists, namely, the publication of new knowledge in chemistry, the Council, as announced in last year's Report, decided to strike at the root of the financial trouble and, by creating the Publications Fund, to establish a capital sum the income of which would ultimately be large enough appreciably to relieve the General Funds of the Society from some of the expenses of publication.

In response to the appeal to Fellows issued in January, 1924, the sum of £1434 17s. 1d. was collected during the year.   Some Fellows, who did not wish to subscribe to a capital fund, gave sums to be expended over a period of years, and of these, the sums assigned to the year 1924, together with the income from the capital fund, have provided an amount of no less than £108 10s. 8d. towards the year's cost of publication.   The Council wishes to record its sincere thanks to those Fellows who have contributed so generously, but it is evident that, if the Fund is to be made really effective, it must be substantially increased, and it is with this object in view that the Council has decided to issue an appeal to Manufacturers.   All Life Compositions are in future to be added to the Fund, which will also be enlarged by the sum of approximately £4000, payable under the will of the late Sir Alexander Pedler.   Nevertheless, until the Publications Fund assumes substantial proportions the need for restriction in the size of the Journal will always exist.   Naturally, the need for the most

stringent care fell within the year under review, and it is due, in a high degree, to the loyal co-operation of authors, referees, and the Editor that the exercise of this very necessary economy has been successful; for the saving on the Journal and Abstracts for 1924 is £796 19s. 6d.

Finally, it will be noticed that the administration expenses are £363 1s. less than those of last year despite an increase in salaries and wages of £29 19s. 6d. This saving is, in a measure, due to a considerable decrease in the item for house expenses and repairs, but it has also been brought about by general economy all round in the administration of the office.

The total savings and additional income for the year from the sources mentioned amount, therefore, to £1994 10s. 7d., and the accounts of the Society accordingly show a credit balance of £210 6s. 10d. despite the fact that there is a fall in the amount of the admission fees for the year of £174 and a decrease of £71 1s. 10d in the amount received for advertisements.

The deficit incurred in 1923 was met by a sale of 3½ per cent. Conversion Stock to the value of £1500, which Stock was purchased on behalf of the Publications Fund, so that, in effect, the total investments of the Society remain the same as those of last year.

Means of increasing the membership of the Society have been explored. Believing that many candidates desiring to join the Society have been deterred in the past from so doing on account of the initial expense, the Council resolved to remit, for a period, the payment of the admission fee. The effect of this policy, which could not be put into force until towards the end of the year, was apparent in that at the December election 114 new Fellows were elected as against 79 in the previous December. Steps have been taken to bring before Chemists who have not yet joined the Society the advantages of the Fellowship, and it is hoped that the policy of the Council in thus remitting the admission fee will be still further justified in the coming year.

In general, therefore, the financial affairs of the Society for the year 1924 present a very different picture from that of the previous year. It is anticipated that another credit balance will be available at the end of the present year, although it must not be forgotten that the Society will lose some £500 of income owing to the remission of the entrance fees. Fellows will not fail to note that this more satisfactory position has been reached without recourse to that increase in the subscription which was foreshadowed in the Report for 1923.

VII. *Research Fund.*

The applications for grants from the Research Fund received during 1924 number 120, the amount for which application was made being £1802, while the amount granted was £844 15s. Owing to the amount applied for exceeding the sum available for distribution, prior consideration has been given to applications received from Fellows. The following grants were made :

	£	s.	d.
The synthesis of a degradation product of strychnine. J. N. Ashley	10	0	0
Addition reactions of styrene with polar reagents. F. Ashworth	5	0	0
The abnormal influence of the *cyclo*heptane ring on the closure and stability of attached rings. J. W. Baker	10	0	0
(*a*) Preparation of β-arylpropionitriles and derivatives. (*b*) Synthetical investigation of the 3-phenylchromane derivatives. W. Baker ...	10	0	0
Study of some aliphatic and cyclic sulphides. G. M. Bennett ...	10	0	0
Photochemical researches (continued) : Relation between quanta absorbed and number of molecules reacting. E. J. Bowen	10	0	0
Hydrolytic fission of methoxy-substituted dibenzoylmethanes. W. Bradley	5	0	0
Co-ordination compounds of beryllium and aminobenzoylacetone. H. Burgess	15	0	0
(*a*) Distribution of organic acids between two immiscible solvents (continued). (*b*) Mobility of the fluorine ion (continued). C. R. Bury and C. W. Davies ...	3	15	0
Investigations on asymmetric synthesis. J. B. Cohen ...	5	0	0
Bismuthyl compounds of the different saccharic acids. J. B. Cohen	5	0	0
Stereochemistry of *N*-acyl derivatives of amino-acids. W. M. Colles	14	0	0
The reversible addition of amines to azo-compounds. K. Cooper	5	0	0
Polymorphic derivatives of benzil. E. A. Coulson	5	0	0
The application of the Guareschi reaction to quinones. R. Craven	5	0	0
Condensation of dioxytartaric acid with various compounds containing nitrogen. R. H. Dilworth	5	0	0
Isomerism and mobility of dihydromuconic systems. W. M. Duffin	10	0	0
Action of diazo-salts on sulphonamides (continued). P. K. Dutt	2	10	0
Chemistry of the aminotriazole derivatives (continued). P. K. Dutt	2	10	0
Relation between colour and chemical constitution. S. Dutt	15	0	0
Investigations on alkaloids and an attempt to synthesise cryptopine. G. A. Edwards ...	10	0	0
Influence of the benzoyl group on the mobility of the three-carbon systems. M. D. Farrow	10	0	0
Steric influence of polymethylene rings on the velocity of reaction in which side chains are involved. R. Gane	10	0	0
Reactions of thiophosgene. H. J. George	10	0	0
Solubility influence. S. Glasstone ...	5	0	0
Determination of physical constants of organo-metallic compounds. A. E. Goddard	5	0	0

	£	s.	d.
Enhanced reactivity of newly formed molecules. F. R. Goss ...	10	0	0
Quasi-aromatic structures. F. R. Goss	10	0	0
Action of halogenating agents on hydroxyanthraquinones (continued). A. Green	5	0	0
Molar complexity of selenium dioxide in alcoholic solution. G. Green	5	0	0
Properties and isomerism of cyclic glutaconic acids. H. Greene	15	0	0
Synthesis of dibromodiethoxythioindigo. Action of acylating agents on substances of an indigoid nature. R. H. Griffith	8	0	0
Attempt to synthesise morphothebaine or its dimethyl ether. J. M. Gulland	8	0	0
Substances derived from methylquinolines (continued). D. Ll. Hammick	15	0	0
Synthesis of amino- and nitro-naphthoic acids. H. A. Harrison	5	0	0
A comparison of the substances obtained by oxidation of cyclopentadiene with the quinones of the benzene series (continued). A. Hassell	10	0	0
Synthesis of alkaloids and allied compounds. R. D. Haworth	10	0	0
Studies in ring formation. A. T. Healey	10	0	0
Action of the alkali metals on simple and mixed ethers. H. Henstock	10	0	0
Synthesis of chloro-o-xylenol (continued). L. E. Hinkel ...	10	0	0
Properties and tautomerism of derivatives of cyclopentadiene (continued). E. L. Holmes	10	0	0
Resolution of antimony compounds of the complex oxalate type. L. H. A. Holmes	5	0	0
Investigation of " Ciba Yellow " and allied substances. E. Hope	10	0	0
Addition of arsenic halide derivatives to unsaturated compounds. A. F. Hunt	5	0	0
Use of aluminium chloride in connexion with the preparation of organic compounds of arsenic. A. F. Hunt	7	0	0
(a) Additive reactions. (b) Mobility of tautomeric systems. C. K. Ingold	25	0	0
(a) Reversibility of additive reactions. (b) Tautomerism of dyads. (Mrs.) E. H. Ingold	15	0	0
The thickness of the adsorption layer on a silica surface. D. C. Jones	5	0	0
(a) Action of formaldehyde and ammonia on nitromalonic ester. (b) Condensation of aluminium ethylate and chloral in carbon disulphide solution. W. I. Jones	5	0	0
Condition of equilibrium between alkali and alkaline earth halides and the alcohols. W. J. Jones	10	0	0
Trivalent carbon compounds. W. J. Jones	10	0	0
(a) Condensation products of monobromo-glutaric and -adipic acids with cyclohexanone. (b) Preparation of unsaturated monomolecular condensation products of cyanoacetamide with various ketones. W. Kilroy	10	0	0
The solubility products of salts in non-aqueous media. F. E. King	10	0	0
Chromammine salts. H. J. S. King	5	0	0
Optically active sulphonic acids. E. E. Mabbot	5	0	0
Properties and structure of a new oxygenated sesquiterpene aldehyde or ketone. F. H. McDowall	10	0	0

	£	s.	d.
Experiments on the formation of nitrones. C. C. N. Vass ...	10	0	0
Attempt to isolate "sulphur sesqui-oxide" and the compound H_2SO or its salts. I. Vogel	5	0	0
The study of nitrobenzaldehyde hydrazones. A. J. Walker ...	5	0	0
Interaction of bromine with acetic and propionic anhydrides (continued). H. B. Watson	10	0	0
Influence of substituents on the formation of ring structures containing nitrogen. R. W. West	10	0	0
(a) Side chain formation in cyclo-paraffins and subsequent synthesis of spiro compounds. (b) Constitution of the mono-chloro- and monobromo-methylsuccinic acids. W. A. Wightman	10	0	0
Temperature coefficient of viscosity of gases. F. A. Williams ...	20	0	0
The effect of the phenyl group on potentially mobile 3-carbon systems. L. T. D. Williams	10	0	0
Total	£844	15	0

A vote of thanks to the Auditors (Professors A. J. ALLMAND, J. S. S. BRAME, and J. F. SPENCER) for their services, proposed by the Treasurer, and seconded by Professor W. E. S. TURNER, was carried unanimously.

Mr. A. CHASTON CHAPMAN proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council, and Committees for their services during the year. This was seconded by Professor C. H. DESCH and acknowledged by Professor J. W. McBAIN.

On the motion of the PRESIDENT, Professors J. F. Spencer, A. J. Allmand, and J. S. S. Brame were elected Auditors for the coming year.

The PRESIDENT then delivered his Address, entitled "Universities as Centres of Chemical Research."

Sir WILLIAM POPE proposed a vote of thanks to the President for his eminent services in the Chair during the past two years and for his Address, requesting him to allow the Address to appear in the Journal. This was seconded by Professor J. C. PHILIP, and carried with acclamation. The PRESIDENT, after acknowledging the thanks of the Society read the report on the election of the Council for 1925—1926 :

President.—Arthur W. Crossley.

Dr. CROSSLEY then took the Chair and after expressing to the meeting his sense of the honour conferred upon him continued the reading of the Report.

Vice-Presidents who have filled the office of President.—H. E. Armstrong, W. H. Perkin, Sir William J. Pope, A. Scott, Sir James Walker, W. P. Wynne.

Vice-Presidents who have not filled the office of President.—J. B. Cohen, A. J. Greenaway, G. T. Morgan, James C. Philip, N. V. Sidgwick, J. M. Thomson.

Treasurer.—J. F. Thorpe.

Secretaries.—T. Slater Price, C. S. Gibson.

Foreign Secretary.—F. G. Donnan.

Ordinary Members of Council.—H. Bassett, D. R. Boyd, O. L. Brady, A. E. Dunstan, F. A. Freeth, F. W. Gamble, W. N. Haworth, C. K. Ingold, J. Kenyon, B. Lambert, H. McCombie, G. W. Monier-Williams, T. S. Moore, B. D. Porritt, F. L. Pyman, J. Reilly, G. Stubbs, F. J. Wilson.

RESEARCH FUND.

Income.	£ s. d.		Expenditure.	£ s. d.
To Dividends on :—			By Grants	844 15 0
£1000 London and North Eastern Railway 4 per cent. 2nd			,, Commission on Recovery of Income Tax ...	3 16 9
Guaranteed Stock	31 0 0		,, Advertisements	4 1 6
£1084 Great Western Railway 2½ per cent. Debenture Stock	20 0 8		,, Cheque Book	1 12 0
£1142 16s. New South Wales 3 per cent. Debenture Stock	34 5 8		,, Longstaff Medal	2 0 0
£1122 Metropolitan Water Board 3 per cent. "B" Stock	33 13 2		,, Award to Medallist (Prof. F. G. Donnan) ...	20 0 0
£853 London, Midland and Scottish Railway 4 per cent.				
Debenture Stock	26 8 10			
£806 Victoria 3 per cent. Stock	18 14 10			
£4408 11s. 0d. 5 per cent. War Loan, 1929/47 ...	224 18 6			
£5527 0s. 9d. 3½ per cent. Conversion Stock ...	181 0 0			
	570 1 8			
,, Income Tax Recovered	76 14 2			
,, Repayment of Grants	177 16 1			
,, Sale of Apparatus	6 11 8			
,, Balance, being Excess of Expenditure over Income,				
carried to Balance Sheet	45 2 1			
	£876 5 8			£876 5 8

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

	£ s. d.			£ s. d.
To Dividends on :—			By Advertisements (Prize)	1 19 6
£500 National War Bonds, 5 per cent., 1928 ...	25 0 0		,, Balance, being excess of Income over Expenditure,	
£500 National War Bonds, 5 per cent., 1929 ...	25 0 0		carried to Balance Sheet	50 3 8
£61 15s. 8d. Conversion Stock (6 months only) ...	2 3 2			
	£52 3 2			£52 3 2

PUBLICATIONS FUND.

	£ s. d.			£ s. d.
To Transfer from General Account, being Life Composition			By Transfer to General Account—Income applicable to 1924	
Fees for year	60 0 0		Publications	108 10 8
,, Subscriptions	115 8 0		,, Balance, being excess of Income over Expenditure,	
,, Donations	1241 10 5		carried to Balance Sheet	1301 10 5
,, Interest on Deposit	17 18 8		,, Subscriptions in advance	24 16 0
	£1434 17 1			£1434 17 1

INCOME AND EXPENDITURE ACCOUNT

Income.

	£ s. d.	£ s. d
To Life Compositions		60 0 0
,, Admission Fees		528 0 0
,, Annual Subscriptions :—		
Received in advance, on account of 1924	585 0 0	
,, during 1924 ,, ,, ...	8425 2 0	
,, ,, ,, ,, 1923	469 2 0	
,, ,, ,, ,, 1922 and previous years	31 18 0	
	9511 2 0	
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	600 0 0	
	8911 2 0	
Add Arrears at date : £811 18s. ; Estimated to realise as per Balance Sheet	500 0 0	
		9411 2 0
,, Investments, Dividends on :—		
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	24 7 10	
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	35 7 4	
£1400 India 2½ per cent. Stock	35 0 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	46 10 0	
£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	84 2 0	
£1200 Leeds Corporation 3 per cent. Stock	27 18 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	45 0 0	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	27 18 0	
£700 Canada 3½ per cent. Stock, 1930/50	18 19 8	
£2100 5 per cent. War Stock	105 0 0	
£1100 5 per cent. War Bonds	42 12 6	
£600 Funding Loan, 4 per cent., 1960/90	21 6 0	
£13854 8s. 3d. 3½ per cent. Conversion Stock	430 7 0	
,, Income Tax Recovered	170 15 8	
,, Interest Received—*less* paid	6 12 7	
		1121 16 7
,, Publication Sales :—		
Journals and Proceedings	2165 4 4	
Abstracts	1614 18 0	
Collective Index, Vols. I–V	133 15 10	
Annual Reports on Progress of Chemistry...	634 4 10	
Berichte and Zentralblatt	60 0 0	
	4608 3 0	
Less Publishers' Commission	413 17 10	
		4194 5 2
,, Proceeds of Advertisements in Journal	623 2 0	
Less Commission	58 13 1	
		564 8 11
,, Miscellaneous Receipts...		56 4 2
,, Donations to Library :—		
Association British Chemical Manufacturers	250 0 0	
Biochemical Society	10 10 0	
Faraday Society	5 5 0	
Institute of Chemistry	250 0 0	
Society of Chemical Industry	100 0 0	
Society of Dyers and Colourists	10 10 0	
Society of Public Analysts	10 10 0	
Research Association of British Rubber and Tyre Manufacturers ...	10 10 0	
		647 5 0
,, Subscriptions from other Societies		23 12 6
,, Transfer from Publication Fund		108 10 8
		£16,715 5 0

FOR THE YEAR ENDED 31ST DECEMBER, 1924.

Expenditure.

	£ s. d.	£ s. d.
By Expenses on account of Journal :—		
Editorial Salaries	770 15 1	
Editorial Postages	53 2 8	
Printing of Journal	3244 4 5	
Banding	64 16 1	
Printing of Advertisements	121 8 3	
Addressograph Labels	5 8 7	
Distribution of Journal	427 1 1	
Authors' Copies	448 4 9	
Insurance of Stock	5 5 0	
		5140 5 11
,, Expenses on account of Abstracts :—		
Editorial Salaries	1198 9 9	
Editorial Postages	31 16 9	
Abstractors' Fees	1063 2 0	
Printing of Abstracts	2824 6 4	
Banding	64 16 0	
Addressograph Labels	5 8 2	
Distribution of Abstracts	427 1 2	
Insurance of Stock	5 5 0	
Miscellaneous	40 11 2	
		5660 16 4
,, Lecture Expenses		52 12 10
,, Advance Proofs and Reports of Meetings		84 11 11
,, Annual Reports on the Progress of Chemistry		661 16 5
,, Purchase of Back Numbers of Journal		13 14 5
,, Library Expenses :—		
Salaries	1188 14 3	
Books and Periodicals	453 1 8	
Binding	127 8 11	
		1769 4 10
,, Donations :—		
Annual Tables of Constants	100 0 0	
Journal of Scientific Instruments	50 0 0	
		150 0 0
Administration Expenses :—		
Salary of Staff	1408 10 0	
Wages (Commissionaire, Housekeeper, and Charwomen)	431 17 6	
Coal and Lighting	75 13 7	
House Expenses and Repairs	114 3 11	
Telephone	23 9 9	
Furniture	18 0	
Tea Expenses	41 10 3	
Insurances	20 11 9	
Accountants' Charges	31 10 0	
Commission on Recovery of Income Tax	8 10 9	
Miscellaneous Printing and Stationery	347 3 1	
Postages	192 5 5	
Legal Charges	13 13 0	
Miscellaneous Expenses	91 17 4	
		2801 14 4
,, Transfer to Publications Account		60 0 0
,, Collective Index Vol. VI*		110 1 2
,, Excess of Income over Expenditure carried to Balance Sheet		210 6 10
		£16,715 5 0

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31ST DECEMBER, 1924.

GENERAL PURPOSES

Liabilities.

	£ s. d.	£ s. d.
To Subscriptions received in advance:— at £3 0 0	1086 0 0	
" Sundry Creditors	2026 18 0	
" Bank Account overdrawn	628 12 1	
" Excess of Assets over Liabilities as per last Balance Sheet	25,449 19 7	
Add Excess of Income over Expenditure for Year	210 6 10	25,060 6 5
		£29,401 11 6

Assets.

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	839 3 7	
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent Stock	1816 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0	
£2718 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4	
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock, 1923-53	1460 13 6	
£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1083 11 0	
£700 Canada 3½ per cent. Stock, 1930/50	704 8 6	
£2100 5 per cent. War Stock, 1929/47	1095 0 0	
£1100 5 per cent. National War Bonds, 1929/47	1045 0 2	
£600 4 per cent. Funding Loan, 1960/90	480 0 2	
£11,873 3½ per cent. Conversion Stock	8987 0 2	
(Market Value £22,584 10s. 4d.)		26,296 3 3
,, Sundry Debtors		2518 11 0
,, Subscriptions in Arrear £311 18s., Estimated to realise		500 0 0
,, Insurance paid in advance		68 11 9
,, Cash in Hand		18 5 9
		£29,401 11 6

RESEARCH FUND

Liabilities.

	£ s. d.	£ s. d.
To Excess of Assets over Liabilities as per last Balance Sheet	14,507 6 3	
Less Excess of Expenditure over Income for Year	45 2 1	14,462 4 2
		£14,462 4 2

Assets.

	£ s. d.
By Investments (value when acquired):	
£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0
£1034 Great Western Railway 2½ per cent. Debentures	1049 15 11
£1142 16s. 0d. New South Wales 3 per cent. Stock	1000 0 0
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9
£853 London, Midland and Scottish Railway 4 per cent. Debenture Stock	1009 18 9
£306 Victoria 3 per cent. Stock, 1929/49	706 6 2
£4498 11s. 0d. 5 per cent. War Stock, 1929/47	4267 4 10
£5827 0s. 9d. 3½ per cent. Conversion Stock	4398 14 10
(Market Value £13,514 6s. 9d.)	14,444 17 3
,, Cash at Bank	17 6 11
	£14,462 4 2

THE EDWARD FRANK HARRISON MEMORIAL TRUST

	£ s. d.		£ s. d.	£ s. d.
To Excess of Assets over Liabilities as per last Balance Sheet	1201 3 0	By Investments (value when acquired):—		
Add Excess of Income over Expenditure for Year	50 3 8	£500 National War Bonds 5 per cent. 1928 ...	500 0 0	
		£500 National War Bonds 5 per cent. 1929 ...	500 0 0	
		£61 15s. 8d. 3¾ per cent. Conversion Stock...	50 1 5	
		(Market Value £1106 3s., 0d.)		1050 1 5
		Cash at Bank		201 5 3
	£1251 6 8			£1251 6 8

PUBLICATIONS FUND

	£ s. d.		£ s. d.	£ s. d.
To Subscriptions received in advance	24 16 0	By Investment £1981 8s. 3d. 3¾ per cent. Conversion Loan		1500 0 0
" Excess of Assets over Liabilities as per last Balance Sheet	235 2 7	(Market Value £1560 7s., 0d.)		
Add Excess of Income over Expenditure for Year	1301 10 5	" Cash at Bank on Current Account	61 9 0	61 9 0
	1536 13 0			
	£1561 9 0			£1561 9 0

W. B. KEEN,
Chartered Accountant,

23 QUEEN VICTORIA STREET, E.C. 4
February 11th, 1925.

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

Approved { J. F. SPENCER, A. J. ALLMAND, J. S. BRAME.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 26th, 1925.

By WILLIAM PALMER WYNNE, D.Sc., F.R.S.

Universities as Centres of Chemical Research.

FOR this, my valedictory address, I have chosen as my text part
of a sentence occurring in the review of the position and prospects
of chemical research in this country with which my distinguished
predecessor, Professor Meldola, closed his period of office in 1907—
seven years before the outbreak of War.   His choice of subject
was singularly appropriate in view of the fact that, in the preceding
year, the Jubilee of the foundation of the coal-tar colour industry
by Perkin had been celebrated at an international gathering in
London, and the occasion seized to emphasise the striking object
lesson thereby furnished of the application of scientific research to
industrial purposes.

Now, in this seventh year after the Armistice, the centenary of
an equally important event—that of Faraday's discovery of benzene
—is to be celebrated.   Rightly and naturally, the Royal Institution
which was the birthplace of this puzzling yet fascinating hydro-
carbon, has assumed responsibility for ensuring due recognition of
its historic discovery.   While we as chemists yield place to no one
in our recognition of the outstanding importance of the isolation
of benzene, none of us will wish to forestall those who assemble in
the historic lecture theatre in Grafton Street on Tuesday, June 16th,
to do homage to Faraday's merit as an investigator and we can
safely leave them to utilise the opportunity of illustrating afresh
the significance of pure chemical research in the progress and
development of chemical industry.

The creation, discussion and publication of new knowledge in
chemistry being the objects for which this Society was founded
and exists, the position and prospects of chemical research in this
country can never be without interest to its Fellows.   Therefore,
at a period removed by almost as many years from the end of the
War as the date of Professor Meldola's address preceded its out-
break, it seems worth while not so much to endorse his indictment
of the conditions which hampered the prosecution of research early
in the century and are not without adverse influences to-day, as to
consider how far, if at all, the outlook for chemical research has
improved during this interval.   I admit the difficulty confronting
anyone like myself who, with a more restricted vision, attempts

to follow a man so eminent in his profession and so well equipped as Professor Meldola was to pronounce judgment on an issue of this kind.   Nevertheless I do venture to think that were he living now, he would be among the first to recognise that the War in changing the face of the world has incidentally altered the estimation in which chemistry is held in this country.

Sir James Dobbie, whose recent death we so much lament, and Sir William Pope have dealt in their addresses from this Chair with the War effort of British Chemistry and shown how true in fact was Meldola's appreciation of its eminence expressed in the words "It is impossible to survey the achievements of our little army of workers . . . . without coming to the conclusion that neither in zeal or originality nor in any of the qualifications which have enabled other nations to advance the cause of chemical science, are we lacking in this country."

This tribute, which the War more than justified, was followed by a discussion of the question whether " the output of work . . . . is really representative of the productive capacity of the nation " leading first to the definite conclusion that " this is far from being the case " and secondly to an analysis of the causes contributing to so unfortunate a result.   Attention was then directed to " the character of the institutions in which research is being or might be expected to be carried on " and, after giving credit to establishments endowed or maintained for the conduct of research, Meldola directed his inquiry to the Universities, University Colleges and Institutions of University rank and to the numerous Polytechnics ·and Technical Schools founded to promote technical education under the Acts of 1889 and 1890.

Quoting again from the address, the opinion is expressed that a few of these institutions of University type " such, for example, as the Victoria University at Manchester, where a recognised school of Chemistry has been created, and Cambridge, whence contributions of importance reach us from time to time, are doing good service in the cause of chemical research."   They, however, are regarded as the exceptions, whereas, judged by the Continental standard, " many of our Universities are distinct failures as centres of chemical research and the total output of work from University laboratories is by no means worthy of the great traditions of this country as a pioneering nation in scientific discovery." ` That the failure of the Technical Schools to advance chemical science should lead to a feeling of profound disappointment need cause no surprise in view of Meldola's long connexion with the`pioneering work of the City and Guilds of London Institute.

In discussing the reasons for this failure on the part of educational

institutions to avoid what he calls " the enormous submergence of research talent " going on in the United Kingdom, Meldola indicates as contributing to it first, the relatively few openings in industry ; secondly, the inadequate salaries paid to assistants and demonstrators ; and thirdly, the inability of promising students to remain after graduation, owing to imperative necessity compelling them to proceed at once from the college to some breadwinning occupation. As counteracting agencies he regards one of the most valuable to be the system of awarding " scholarships to men of approved ability to enable them to carry on original work after finishing their college training " and refers specifically to the Scholarships given by the Royal Commissioners of the 1851 Exhibition, by the Salters' Company and by the Carnegie Trust for the Universities of Scotland.

With your permission, I propose to examine these conclusions— not in any spirit of criticism but with the sole object of considering how far they apply to post-War conditions and what additional remedies, if any, can be suggested to check, if not prevent, the wastage of the research faculty.

Output of Research from Universities and Technical Colleges.

In the first place some estimate must be formed of the output of research from Universities and kindred institutions on the one hand and from Technical Colleges on the other. If based, as seems inevitable, on the number of chemical papers published from their laboratories, the list must include purely theoretical discussions, which may vary in importance, as well as contributions dealing with new experimental work. Moreover, the discrimination of papers which seem to be purely physical, physiological or metallurgical in outlook is not free from difficulty unless regard is had to the Department to which the contributor is attached. With these considerations in mind, the following table has been compiled as the result of a scrutiny of the papers published in the journals indicated :

Summary of Chemical Papers published from Universities and Colleges of the United Kingdom during the three six-year periods : 1901—06 ; 1908—13 ; 1919—24.

	Trans.* Chem. Soc.	Proc. Roy. Soc.	Faraday Soc. Trans.	J. Soc. Chem. Ind.	J. Amer. Chem. Soc.	Total.
1901—06	747	107	—	11	0	865
1908—13	1132	75	38	25	1	1271
1919—24	1268	56	45	70	25	1464

* The total number of papers contributed to the Transactions from all other sources during these six-year periods was 226, 359 and 406 respectively.

Distribution of these Papers.

	1901—06.	1908—13.	1919—24.
Oxford University	18	89	140
Cambridge University	82	122	142
Manchester University	91	139	84
Imperial College (R.C.S. and C.T.C.)	101	114	143
Percentages	33·8	36·5	34·8
London University Colleges and Medical Schools (13) *	161	244	206
Modern English Universities and University Colleges (11) †	197	252	375
Welsh University Colleges (3)	28	42	47
Scottish Universities (4)	68	85	154
Irish Universities and Colleges (6)	46	53	40
Percentages	57·8	53·2	56·1
Polytechnics and Technical Colleges (20) 73	131	133	
Percentages	8·4	10·3	9·1

* Excluding Imperial College.
† Excluding Manchester University.

Of the deductions that can be drawn from these figures there is one which we, as chemists, cannot but regret, remembering the conspicuous part played by Sir Henry Roscoe, first in promoting two Bills for assisting technical education which failed to reach the Statute Book and, afterwards, in aiding the passage through the Commons of the Technical Education Acts to which reference has already been made. If, as seems to be the case, there are some 180 Technical Schools in the United Kingdom,* financed under the provisions of those Acts and equipped with Chemical Departments, and 90 per cent. of them have failed to contribute a single original paper to any of the journals quoted during the period under review or previously, it is evident that their failure to prosecute chemical research has become stereotyped. When it is remembered that the staffs of these schools include chemists who before appointment had shown themselves imbued with the research spirit and, given the opportunity, would doubtless have diffused it among their colleagues, this sterility must be attributed not to them but to the conditions under which their work is done. The conclusion to my mind is inevitable that in the opinion of the great majority of the governing bodies of these Institutions the terms " technical education " and " trade school training " are synonymous at least so far as chemistry, pure or applied, is concerned.

It is the University contribution, however, with which this address is chiefly concerned. Inspection of the table will show

* Cf. " Official Chemical Appointments, 1924," pp. 86—113, issued by the Institute of Chemistry.

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that the year 1914, which was more prolific than 1913, has been
omitted together with the four War years, but 1919, almost, if not
quite, the worst, is included in the last six-year period.   Its inclu-
sion may serve to balance the abnormal research activities of the
later years, particularly in view of the fact that the peak in the
graph of the number of papers plotted against years seems already
to have been passed.   Taking the figures as they stand, it is evident
that in measuring the effort of the other Institutions in terms of
the productivity of Manchester and Cambridge, Meldola under-
estimated the research output of the United Kingdom in the years
preceding 1907.   On the other hand, it is clear that the improve-
ment which he descried in comparing successive decades has
increased by 47 per cent. and 69 per cent. when the two later periods
tabulated are compared with the first.

The approximation to uniformity with which each of the three
groups in the table has maintained its position, notwithstanding
these increases in the total number of papers published, is acci-
dental, but in three cases only, and these in the difficult post-War
period, is there any departure from the steady rise in productivity.
The apparent uniformity, however, is not without interest, even if
unexpected, and may be construed to mean that the Chemistry
staffs of these Institutions, including those shown in the last line,
realise fully the value and importance of research as an adjunct
to teaching and within the means at their disposal cultivate it
assiduously.

Causes restricting the Output of Research in Universities.

I turn now to consider the question whether these means are
adequate or whether in Meldola's words there is not still " much
work ahead of us before the environment in which our workers
find themselves is properly cleared from obstruction."   The modern
Universities have in nearly every case sprung from University
Colleges and these in a more remote past from Colleges to which
the Founder's name more often than not was attached.   These
Institutions in their early days experienced many difficulties, of
which the endurance of poverty was by no means the least.   Readers
of Sir William Ramsay's life will remember how many of them
were barely saved from extinction by the opportune grant of a
subsidy from the Government which in course of time has grown
to be £1,500,000 and is shared in now by Oxford and Cambridge.
One result of that early penurious existence was the inevitable
tendency on the part of the administrative bodies to judge the
success or the need of a department by the number of students
working in it and another, the disposition to regard all departments

as of equal value or importance. If to both of these impediments be added the relatively high maintenance cost of laboratory provision and upkeep, it will be no matter for surprise to the historian of the last 50 years that the long and arduous struggle to surmount these traditions is not yet over.

How welcome it would be, for a change, if financial circumstances rendered it possible for inquiries to be more often directed towards the number of postgraduates engaged in research or made with reference to the number of hours per week during which each member of the staff is able to pursue research. Teaching, in the sense of training students for a degree, is not the only function of a University—the Statutes of the newer Universities leave us in no doubt on the point even if assurance be needed. Beyond such teaching, all important as it is, lies the training of the postgraduate which will always be the more difficult of the two if conducted, as it surely ought to be, in the spirit so admirably portrayed by Principal Sir James Irvine in the following extract from his address to the Chemical Section of the British Association meeting at Hull :

" There are few more harassing duties than those which involve
' the direction of young research chemists. . . . I am well aware
' that scorn has been poured on the idea that research requires
' training. . . , Individual attention is the first necessity and the
' educative value of early researches is largely derived from the
' daily consultations at the laboratory bench or in the library. Many
' research supervisors find it difficult to enter sympathetically into
' the mental position of the beginner, yet if the pupil is to derive any
' real benefit from his difficulties, his adviser must for the moment
' place himself in the position of one equally puzzled, and must lead
' his collaborator to sum up the evidence, and arrive at the correct
' conclusion for himself. The policy thus outlined is, I believe,
' sound but it makes severe demands on patience, sympathy and,
' above all, time. Research supervision, if conscientiously given,
' involves the complete absorption of the director's energy and
' leisure."

The Arts Faculty is the most numerous and usually the best organised in our modern Universities. Its members have no personal experience of laboratory teaching, inseparable from curricula in science subjects, pure and applied including medicine, and can devote to their own intellectual pursuits the hours which in our Departments it consumes. Were equality of treatment afforded to both sides of University life, the limitation of teaching duties to part only of the working day rightly conceded to our Arts colleagues would, if accorded to laboratory subjects, give to the research side

of our work not odd hours or half days but the equivalent of all the afternoons. Until this becomes the normal feature in laboratory subjects, with the corollary of increased staffs to make it possible, we must not slacken in our educative effort to secure such recognition for our work.

Who does not know and sympathise with the dilemma with which the younger members, shall we say, of the staff of a Chemistry Department are confronted, well knowing that the avenue to promotion is research and yet reasonable opportunities for its pursuit cannot be provided, owing to the financial embarrassments by which University efficiency is retarded? Is the training of undergraduates to suffer, so that research may be kept going, or is the zeal for research to wane until the 'thirties come when its spirit, once damped, is difficult to rekindle? It is this " submergence of research talent " within the Universities themselves which needs first to be remedied.

Whether, under post-War conditions—when the call for economy becomes more, not less insistent—such an increase in Staffs as would be required to equip adequately the research laboratories of our Universities can be provided is more than doubtful, but none of us can regard the present position with any degree of satisfaction. Those who make the quinquennial visitation of Institutions of University rank in connexion with the allocation of State aid are perhaps less accessible to representations from heads of Departments than before the War, but they cannot be in any doubt about the magnitude of the problem with which University education may soon be confronted. It is nothing less than this—can each of the modern Universities, without reference to its neighbours, continue to teach all subjects to the same level and yet remain efficient as contrasted with Continental or American Institutions? The question might still be asked even if they were adequately endowed, which they are not. In the present straitened circumstances, is there any more prudent course than for each to strive for the utmost possible development of a restricted number of subjects in pure or applied science and to be content with a less complete provision for the remainder? In the fierce competition of the modern world—to aid our country in facing which is not one of the least important functions of University training—as in War, nothing lower than the best is of any avail. The problem is : Are we in a position to meet the ever-increasing demand for more intensive study and research in the domain of pure and applied science without either ample endowment, of which there is no prospect, or a radical change of policy in which the good of the community must overrule individual susceptibilities and local pride ?

Postgraduate Research Scholarships.

I have dealt with some of the difficulties which handicap the research output of University staffs. Without research students, the handicap would be largely prohibitive. Apart from those in whom the desire to become investigators is inborn, research students are attracted either by the prize of a higher degree or by the prospect of finding employment which experience of research may afford. Without the provision of Scholarships, these opportunities are denied to graduates whose parents cannot afford the cost of maintenance during an additional period of non-remunerative work. Yet experience shows that in many cases it is this type of student which, given the opportunity, makes the most of it, benefiting alike his country and himself. As the position with regard to the provision of research scholarships has undergone important changes within the last ten years, a brief summary of the conditions attached to, and the results achieved by, the three Scholarship schemes mentioned by Meldola may not be out of place.

The 1851 *Exhibition Scholarships.*—First in point of time was the generous scheme of scholarships, and later of bursaries, established by the Royal Commissioners of the 1851 Exhibition. Inaugurated in 1891, this effort represented only one aspect of the Commissioners' promotion of Science, Art and Industry. It continued in operation, so far as Science Scholarships were concerned, until 1915, was resumed in 1919 and placed on a new basis in 1922. Under the scheme, each modern University in the United Kingdom, together with certain University Colleges and Dominion Universities, was invited to nominate a candidate for a scholarship of £150 * a year, tenable for two years and renewable in approved cases for a third. If the Commissioners were satisfied that the graduate nominated had given " distinct evidence of capacity for research " the scholarship was awarded to enable him " to continue the prosecution of science with the view of aiding its advance or its application to the industries of the country." To it was attached one most important condition : the Scholar was " required, in absence of special circumstances, to proceed to an Institution [at home or abroad] other than that by which he was nominated." In 1900, bursaries of £70 † tenable for one year were founded to enable graduates in science with honours to obtain a year's training in research so as to qualify for a scholarship. Through the kindness of the Secretary to the Commissioners, I have had access to the records for the years 1891 to 1921, from which the following tables have been compiled :

* Raised in 1919 to £200 and in 1921 to £250.
† Increased in 1919 to £100.

(i) Distribution of 1851 Exhibition Scholarships among Modern Universities, University Colleges and Dominion Universities.

	English.	Welsh.	Scottish.	Irish.	Dominions.	Total.
1891—1914 (24 years)	197	22	62	36	99	416
1919—1921 (3 years)	18	6	5	6	20	55
	215	28	67	42	119	471

(ii) 1851 Exhibition Scholarships awarded in Chemistry, 1891—1914.

	Total number awarded.	Number awarded in Chemistry.	German doctorates in Chemistry gained by Scholars.
United Kingdom	317	157	77
Overseas Dominions	99	30	18

From these data, it is obvious that practically one half of the Scholars were chemists, all of them migrants from the Universities which trained them and many adding to the stimulating experience of a new environment the knowledge of another people and another language. It has been an interesting study to note how many of our University staffs have been recruited from among these scholars. Recalling the figures shown in the first table, it can be no mere coincidence that the increased output of research synchronises with the development of this scholarship scheme—rather, the two are related as effect and cause. The same view, probably, would be endorsed in respect of research in each of the subjects other than Chemistry aided in like manner by the Commissioners of the 1851 Exhibition.

Since the War, owing partly it may be to the alteration in the value of money and partly to the operation of another scheme of more recent date for the training of research students, these scholarships have been replaced since 1921 by a smaller number, carrying a grant of £300, designed to enable the investigator with three or four years' research experience to his credit to continue working for an additional period without the distraction of teaching or other form of employment. Scholarships of this type, such as the Beit Fellowships or those associated with Sir William Ramsay's name, have become more frequent since the War, and already have justified their inception as aids to research.

The Carnegie Scholarships.—Whereas the Research Scholarships of the 1851 Exhibition have been open to all Universities, those awarded under the Carnegie Trust established in 1901 are limited to Scottish graduates nominated by Professors or Lecturers in Scottish Universities. The scheme comprised scholarships of the value of £100 * tenable for one year but renewable, if deemed

* Now £75.

expedient, for a second year, and Fellowships of the value of £150 * tenable for two years. Unlike the awards of the 1851 Exhibition these scholarships and fellowships can be and for the most part are held in the University in which the holder has graduated. The facts set out in the following table have been collated from the Official Record of the work of the Trust during the first two decades of its operation 1903—1923, published last year, with a copy of which I have been furnished by the kindness of the Secretary of the Trust :

Distribution of Carnegie Scholarships and Fellowships.

Total number of individuals elected to Scholarships and Fellowships (1903—1923) 375

Total number of Scholars and Fellows in Chemistry 105

The number of these Scholars who did not proceed to Fellowships was 72

The number of these Fellows appointed, 20 of whom had previously held Scholarships, was 33

The number of individual Scholars and Fellows who published research work was 72

The number of papers published by them was
        (a) In one name .... 65 (16 abroad)
        (b) In two or more names 137 (8 abroad)

No words of mine are needed to emphasise the value and importance of the work of the Carnegie Trust; all branches of learning are fertilised by its aid, but Chemistry as would be expected receives the largest amount of assistance.

The Salters' Company's Fellowships.—Although necessarily conceived on a much smaller scale than either of the preceding schemes, the fine effort of the Worshipful Company of Salters has been no less successful in promoting research. The earlier scheme, initiated in 1894, provided three Research Fellowships in Chemistry, two of the value of £150 each, of which one was attached to the City and Guilds Central Technical College, and the third of £100. Having served its purpose, it was replaced in 1918 by the foundation of the Salters' Institute of Industrial Chemistry, designed, among its objects, to enable post-graduates with some experience of research to undergo further training for a career in Industrial Chemistry, the Fellowships awarded to this end being normally of the value of £250—£300.†

Establishment of the Department of Scientific and Industrial Research.

During the War, as already indicated, the 1851 Exhibition scheme fell into abeyance and now has been based on an entirely

* Now £250.

† It may be of interest to record the fact that Dr. M. O. Forster, whose services to the Society as Secretary and as Treasurer are gratefully remembered, was in 1894 the first Salters' Fellow at the Central Technical College, and in 1918 the first Director of the Salters' Institute.

different footing, but, most fortunately, there was founded in 1915 an organisation the activities of which are well defined by its title—I refer to the Department of Scientific and Industrial Research. In creating the opinion which led to the establishment of the Department, Fellows of this Society may claim to have had their part. In 1915, Sir William Crookes was President of the Royal Society and under his Chairmanship a meeting of chemists was held in that Society's rooms on February 2nd, followed by two meetings, with Professor Meldola in the Chair, on February 15th and March 10th, at which the serious position facing the chemical industry was discussed, a memorial to the Government prepared and an interview sought with the Prime Minister. At the interview on May 6th, 1915, the Ministers present being Mr. Runciman, President of the Board of Trade, and Mr. Pease (now Lord Gainford), President of the Board of Education, some 20 chemists, grouped as representatives * of our own Society (including its President, Dr. Scott, and the officers), and of the Royal Society, introduced by Sir William Crookes, advocated not only the formation of a Central National Advisory Committee, composed mainly of chemists and chemical manufacturers, to recapture the lost chemical industries but also the importance of research in connexion with any such effort. After speeches in support of the memorials submitted, Mr. Pease announced that the Government had consented to the preparation of a scheme for aiding research work, and on July 23rd, 1915, Mr. Arthur Henderson, who had succeeded him as President of the Board of Education, issued the " Scheme for the organisation and development of scientific and industrial research " as a white paper. In this historic document the opening statement runs :

" There is a strong consensus of opinion among persons engaged ' both in science and industry that a special need exists at the ' present time for new machinery and for additional State assistance ' in order to promote and organise scientific research with a view ' especially to its application to trade and industry."

Eighteen months later, on Friday, December 1st, 1916, Lord Crewe announced to a deputation consisting of some 150 representatives of science pure and applied, meeting in the hall of the Institution of Civil Engineers, that the work of the Committee of the Privy Council for Scientific and Industrial Research and that of its Advisory Council (of which Professor Meldola himself was an original member), associated from its inception with the

* Including a Vice-President of the Institute of Chemistry (in Professor Meldola's absence through illness), the President of the Society of Chemical Industry and the President of the Society of Public Analysts.

Board of Education, had been established as a separate Government Department. From that time onward, provision for scientific and industrial research has been recognised as a duty incumbent on the State. Although, as is the habit of our countrymen, there has been criticism of the work of the Department, I think all who are in a position to pass a considered judgment will concur in the view that, whether it be in the promotion of research associations to aid industry, or in the provision of maintenance grants for the training of graduates in research methods, or in the support of national institutions transferred to its care, the D.S.I.R. has done a service to science and the country so great as to be almost incredible in the light of pre-War neglect.

If attention be confined to the grants made for research training in those branches which have industrial applications, it will be found that the annual expenditure from 1920 onwards has been between £40,000 and £50,000; the table shows, in part, the results achieved which are embodied in the annual reports of the Department to Parliament :

| | Total number of grants. | Grants for chemical research made to | | Number of published papers recorded by the Department in | |
		graduate students.	independent workers and Research Assistants.	all subjects.	Chemistry.
1919—20	109	29	22	40	13
1920—21	202	95	20	122	65
1921—22	260	135	20	143	78
1922—23	290	145	11	126	80
1923—24	279	141	14	152	88

The D.S.I.R. warns us that the provision of maintenance allowances for training in research must not be regarded as a permanent feature of its activities, but it may well be hoped that the date of this withdrawal lies in the remote future, unless provision is made by the State for Universities themselves to bear the cost. It is unquestionably the case that to the provision of these grants is due the rapid revival of research schools after the War, nor can we lose sight of the fact that those students to whom a renewal of the grant for a second year has been made have thereby been enabled to qualify by residence for the Ph.D. degree.

Institution of the Research Degree of Doctor of Philosophy.

The institution of the Ph.D. degree was itself a War measure. In view of the likelihood that German Universities would not be frequented by students from the Allied or Associated countries until after the lapse of an interval of years from the making of

Peace, inquiries were set on foot towards the end of 1916 through the Foreign Office and the Board of Education to ascertain whether British Universities could make provision for research students from America or the Overseas Dominions who, normally, would have studied in Germany. Such provision, it was recognised, would involve the institution of a research degree corresponding with the German Doctorate of Philosophy. As the outcome of conferences and discussions, these Universities in May, 1917, agreed in principle with the view that postgraduate research leading up to a degree should be organised for home or overseas students. A year later they approved the draft ordinances for the new research degree of Ph.D. It is not wholly without interest to recall the pleasure with which their representatives on the previous day had received from Mr. Balfour (now Lord Balfour) at the Foreign Office an assurance of his satisfaction at the steps contemplated " to make attendance at our Institutions more attractive to students from the United States, France, Italy and other Allied countries." Those steps, need it be said, would have involved the expenditure of large public funds if our modern Universities were to be put in a position to furnish the equipment and offer the amenities to which American and Overseas students are accustomed. Any hope that such steps would be taken foundered—like many another hope of that time—in the economic storm which followed at no long interval in the wake of the War.

This failure to provide travelling scholarships brought about a difference in status between home and overseas candidates which ought not to be overlooked—those at home are not required to leave the University in which they have graduated while carrying out research for the doctorate. We, in Sheffield, at the first of the conferences just mentioned, urged that the research work of all candidates for the Ph.D. degree should be conducted in a second University, as was necessarily the case with those 1851 Exhibition Scholars who obtained the German doctorate. The proposal received little or no support and has not been revived. One objection, widely entertained, was to the effect that such a condition would operate harshly in the case of otherwise excellent students who, in the absence of adequate postgraduate scholarships, could not find the means to enable them to live away from home during the minimum period of two years' research training required for the degree.

Yet, from the student's point of view, who can doubt the great advantage accruing from the opportunity of working in a different environment during the last years of his training? Other things being equal, which of the alternatives will give the research student

the more valuable experience—to stay in the laboratories in which he has pursued his Honours course, or to have a complete change in surroundings ? In the one case, the attitude of teacher to student and *vice versa* is unlikely to suffer much change, but in the other—there being no link with the immediate past—supervisor and postgraduate can begin their co-operation from an entirely different standpoint. Beyond all question, what is needed among research students and those promoted therefrom to junior staff appointments is a wider experience than can be gained by living in the atmosphere of one laboratory, associated with the same teachers and fellow students, during five or six years. In interviewing candidates for higher posts there is nothing arouses more regret than this want of experience—from which before the War the Commissioners of the 1851 Exhibition provided some way of escape.

As there is no immediate prospect that any step can or will be taken by British Universities to meet this defect—as surely it is—in the regulations for the Ph.D. degree, the question is worth asking : Cannot a solution of the difficulty be found in another way ? Under Mr. Fisher's guidance, the Board of Education instituted a series of State scholarships, planned on novel lines, to Universities, thereby adding to the large number of entrance scholarships already in existence. Until the D.S.I.R. set on foot its admirable scheme of grants for research, the State had done nothing to help the graduate forward in his career. As is the case with the State scholarships, these grants are based on the financial circumstances of the applicants; reasonable certainty therefore exists that the provision of State aid is not abused by those who have the necessary means. How far it may be wise to hazard the suggestion I do not know, but the problem would be solved if, the first year's training (following immediately on graduation) being given in the graduating University (as was the case with the 1851 Exhibition Bursars and is permitted to the Carnegie Trust scholars), it were made a condition of renewal that the grantee migrate to another Institution. If further the renewal, in approved cases, could be extended to a third year and the maintenance grant increased during the one or two years' absence from home, I am convinced that the benefit to Chemistry, or to any other branch of science aided by the Department, would be not less pronounced than that associated with the 1851 Exhibition Scholarships.

Chemists no less than other scientific men are prone to be conservative in their outlook. It may be that the effect of any such change in research training might operate at first to the disadvantage of the smaller and less well equipped Universities—such a

possibility should, I venture to think, be accepted. It would at least furnish a criterion of relative efficiency which Governing Bodies could take to heart. In Germany before the War, entry into certain schools was more eagerly sought by research students than into others. If Germany could accept that position and did, why should we be reluctant to face it ? If support be forthcoming for the view I have advocated, it is permissible to hope a way will be found to encourage the migration of students. How can it be otherwise when we remember that the outlook for the student of to-morrow and for Chemistry depends on the equipment of the student of to-day ?

Openings in Industry for the Research Chemist.

I now turn to another point on which Professor Meldola touched in his Address—the existence of relatively few openings in chemical industry for the trained research chemist. Here, too, it is possible to recognise a change in outlook, despite the fact, which we all deplore, that acute depression in trade in 1920 and subsequent years led to a large amount of unemployment among industrial chemists and thus limited the opportunities of finding openings for postgraduates newly trained in research. Regrettable as this is, it can no longer be referred directly to apathy on the part of industrial firms, and for this reason. The D.S.I.R. was founded in 1916 not only to fulfil the valuable function of training University graduates in research but for the express purpose of stimulating industry by the foundation of research associations which by their example would in turn convince the respective industries of the supreme importance of research if trade is to be maintained in the face of intense, unresting competition.

These research associations, largely composed of manufacturers and in part financed by them, have in many cases had their original period of five years renewed, and incidentally have provided opportunities for research workers who presumably will be absorbed in the respective industries covered by the research associations. Moreover, it must be clear that for full advantage to be taken of the reports furnished by such associations, it is inevitable that an intelligence department manned by research workers must be installed in works which propose to utilise the information circulated to the industry concerned. In these respects, undoubtedly, the D.S.I.R. has laid industry under no less an obligation than academic work and done much to secure an outlet for the research worker trained in Universities and University Colleges.

But, repeatedly, the objection is urged by manufacturers that the University-trained product is of little use to them, is not

adaptable, cannot handle men, and becomes dissatisfied if the reforms which seem so obvious to him in the management of a works do not commend themselves forthwith to those in charge. And there is the innate idea in the minds of many that they should go into the research department or the control laboratories, rather than work their way up through the factory if called upon to do so.

If these faults exist, is it not at least possible that the University-trained man is not wholly to blame ? What opportunity is afforded him of testing his vocation for industrial work ? In the University, as at school or on the playing field, he has tested himself against his fellows under the only conditions known to him, and has formed some measure of his capacity to cope with the problems that arise in connexion with them. Transferred to a works, he needs time for readjustment to the new environment and during that period doubtless displays something less than the wisdom born of experience and age. The University trains the chemist and on the thoroughness with which that training has been applied to educate mind and eye and hand, its reputation as a chemical school depends. What does chemical industry do for the man who wishes to enter industry by way of the University ? Does it afford him any opportunity of testing his vocation while there is yet time for him to make another choice ? Does it help him in any way ?

Before the War there was small opportunity for highly trained chemists to find their way into industry. Usually, the works trained their own chemical assistants who by the aid of evening classes and their own grit became efficient instruments for routine work. But that system is not likely to prove very helpful in the face of competition with America or Germany, where a better appreciation of the value of systematic training is found in the close relationship between University and factory. University and Industry—theory and practice—obviously must collaborate if the chemical industry of this country is to make headway in face of present difficulties.

Vacation Experience for Students in Chemical Works.

Early in 1917, the great corporation known as the Association of British Chemical Manufacturers came into being as the result, primarily, of action taken by the Council of this Society two years earlier in constituting itself a consultative body on all chemical matters arising out of the War. The history of the conferences and negotiations set on foot with the Councils of kindred societies and other bodies, which led to the formation of an industrial federation

unique in British chemical industry, has yet to be written.   But
our share in it emboldens me to ask whether it is not possible for
some at least of the larger firms in the Association to allow
selected students from Universities in their neighbourhoods to spend
some part (say two months or ten weeks) of each Long Vacation
in their works, not necessarily in laboratories but under foremen
on the plant, working under factory conditions and thus becoming
aware by actual experience of the kind of mental equipment required
to deal with the problems that arise in connexion with large-scale
working ?

Two objections may be raised—the first that secret processes
would no longer be protected and the second, that young students
introduced into works in the way suggested would cause too much
trouble, or their inexperience interfere too seriously with the routine.
In reply, I can say that in Sheffield this problem has been faced
and solved : it is the custom for intending graduates in Metallurgy
to spend part of the Long Vacation in certain of the steel works in
the City, to be welcomed there and to be placed under foremen to
do such work as may be suggested.   If this is possible, and there
is this close association between the applied chemistry of the
Metallurgical school and the steel works, in which secret processes
if they exist anywhere would be likely to be found, is it too much
to hope that something of the same kind may be introduced into
chemical works for the good of all concerned ?   The works would
be able to pick their men in course of training and, doubtless, the
University studies of such picked men after graduation could be
directed to the type of work which would be of use later on.

I am fully aware that industrialists, managing directors among
them, assert in no uncertain tones that the Universities do not know
how to train men to be of use to them.   To my mind the criticism
is just as helpful or the reverse as that pronounced by University
professors who assert with equal confidence that the works, through
lack of scientific control, are courting the fate which in their view
deservedly awaits them.   Such pronouncements carry us nowhere :
what is beyond measure needed is some scheme of co-operation
with a real intention and endeavour to devise a means by which the
University may become more helpful to the manufacturer and the
manufacturer to the University.   United, I feel sure we can face
the world—divided and unhelpful the one to the other, we shall
have done nothing, despite the lessons of the War, to improve
upon the state of things to which Professor Meldola made such
regretful allusion.

Community of Interests among Chemists.

I have assumed that this Society represents more the University or academic side of chemistry and the A.B.C.M. the industrial side. Between them is found that vigorous body of industrial chemists, the Society of Chemical Industry, and its President, Mr. Woolcock, is, as we know, the Manager of the A.B.C.M. He will forgive me if I suggest that the moment is propitious for an advance to be made and that during his Presidency he will render chemistry a lasting service if he can take the first steps towards promoting a closer working between the two sides—a better appreciation of one another's difficulties and a sincere attempt to resolve them. The Pure Chemistry exhibit in the Wembley Palace of Industry owed much to his genius for overcoming difficulties. I allude to it not merely as showing that pure chemistry, like applied chemistry, can enter into association for the common good, but rather to draw attention to the fact that the Pure Chemistry exhibit was separated by a partition from its applications in industry—chemistry pure and applied being separated by a screen. True there were openings from the one side to the other, but they were small in comparison with the area covered by the screen—and to my mind that screen symbolised " the middle wall of partition " between the two sides of chemistry, which perhaps no one person could take more effective steps to break down than my brother President, who by singular good fortune happens to be a member of the three bodies concerned.

In its approach to the Society of Chemical Industry, leading up to the foundation of the Bureau of Abstracts and to co-operation in other directions, this Society has shown itself willing to go some part of the way towards a closer community of interest—the future alone can show whether these and other like efforts will have their fruition in the development of a corporate union of chemical interests, which shall ensure for chemistry the recognition which is its due in the national estimate of the importance of science in promoting the welfare and progress of the Empire.

I cannot sit down without expressing my sincere thanks to the Officers, Council and Fellows of the Society for the kindness shown by them during my period of office; to Mr. Carr, Mr. Clifford and the house staff for assistance rendered readily and willingly at all times, for which I cannot find words wherewith adequately to convey my appreciation; and to the members of my staff at Sheffield who have made it possible for me to maintain the tradition that the President should be in the Chair at all meetings of the Society. That the same kindly feeling may be extended to my successor is a request which I am sure is granted even before it is

made—he brings to the office much experience gained on the one hand in the conduct of its affairs as Honorary Secretary and Foreign Secretary, and on the other in academic life, in the Army, and now as Director of one of those important research associations to which reference has been made. In view of such a record, we may indeed feel sure that the great traditions of this Society will be safe in his hands.

OBITUARY NOTICES.

GEORGE THOMAS BEILBY.

BORN NOVEMBER 17TH, 1850 : DIED AUGUST 1ST, 1924.

GEORGE THOMAS BEILBY was born in Edinburgh, where his father was in practice as a physician, and was educated at private schools and at the University of his native city. In 1877 he married Emma, daughter of the Rev. S. Newnam, by whom he is survived, as also by a son, Hubert N. Beilby, who is technical director of the Cassel Cyanide Company, and a daughter, the wife of Professor Soddy.

In 1869, at the age of nineteen, Beilby entered upon an industrial career of remarkable success by accepting a post as chemist with the Oakbank Oil Company, and very soon after his appointment proceeded to give proof of the originality and skill as an investigator which he continued to manifest during the whole of his working life. He attacked the problem of the distribution of the nitrogen in bituminous shale when it is distilled for the production of paraffin oil, and a long series of laboratory and large-scale experiments, carried out largely by himself and partly in collaboration with William Young, resulted in the introduction of improvements in plant and in methods of manufacture which gave a new lease of life to the paraffin oil industry in Scotland. A brief account of this work is contained in an important paper " On the Production of Ammonia from the Nitrogen of Minerals," which he contributed to the Glasgow Section of the Society of Chemical Industry in 1884, and was the first of a large number of memoirs on scientific and technical subjects communicated to the Royal Society, the Chemical Society, the Society of Chemical Industry, the *Philosophical Magazine*, the *Reports* of the British Association, etc.

For a number of years Beilby carried on invaluable work in this field of industry, but after the introduction of the cyanide process for the extraction of gold he directed his attention to the discovery of new methods for the production of alkali cyanides. In 1891 he patented a process which was set in operation, under his care, by the Cassel Cyanide Company and developed into a large and successful industry.

Certain observations made in connexion with his cyanide process led Beilby to enter upon the series of brilliant investigations into the physical properties and especially the microstructure of metals and other solids in different states of aggregation, which he continued

to prosecute until near the end of his life. The results of these investigations, many of which had an important bearing on metallurgical problems, are summed up in a masterly volume on " The Aggregation and Flow of Solids " which he published in 1921.

From the very beginning of his industrial career Beilby took the keenest interest in the question of fuel economy. He made a special study of this subject, and in 1903 presented an exhaustive report to the Royal Commission on Coal Supplies, in which he emphasised the enormous waste of coal in this country, with the attendant production of smoke and dirt in our large cities, through inefficient combustion. In 1912—1913 he served on Lord Fisher's Committee on Fuel and Engines for the Navy, and the conclusions arrived at by that Committee were largely based on the great amount of pioneering experimental work on low-temperature carbonisation which had been carried out under his direction in the works of the Cassel Cyanide Company. The importance of this subject led to the establishment, in 1917, of the Fuel Research Board by the Department of Scientific and Industrial Research, and Beilby, who was already a member of the Advisory Council, was appointed Chairman and Director of Research. He held this post until he found it necessary to retire in 1923, and the value of his services is attested by the following tribute paid to him by the Committee of the Privy Council for Scientific and Industrial Research :

" to him the creation of the necessary organisation and the design and building of H.M. Fuel Research Station at East Greenwich are solely due. He, more than any other man, put the scientific knowledge of low-temperature carbonisation on a firm basis; his work on gas standards had a formative influence on recent legislation for the gas industry, and his skill as a microscopist opened up a fascinating direction for research into the structure and behaviour of coke. It is with the deepest regret that we lose his wise and experienced counsel and the great scientific and practical knowledge he brought to the many difficult questions with which the Department in the early years of its existence had to deal. We desire on behalf of the Government and the nation to place on record our high appreciation of all that he so generously and freely gave them both during the War and in the hard and critical years which have succeeded it. Through all, his aim and effort were to help to the utmost the re-establishment of this land and people."

It should be added that during the War Beilby took an unremitting and highly esteemed part in the activities of the Trench Warfare Committee and the Naval Board of Invention and Research.

Beilby also took a deep and active interest in educational matters. In 1907 he was elected Chairman of the Governors of the Royal Technical College, Glasgow, and remained in office for sixteen years. His scientific attainments, his capacity for organisation, and his enlightened generosity were of the utmost importance to the College during the most active period of its development, and his sympathy with the members of the staff in their efforts to augment the opportunities for the prosecution of research work in each department took a very practical form. He was a strong advocate of technical education and always emphasised the necessity of securing the co-operation of the leaders of industry in modelling technical institutions. Impressed as he was with the importance of the fuel question, soon after his appointment as Chairman he arranged for the equipment of special laboratories in the College for instruction and research in fuels, these being the first of their kind in this country.

Beilby's eminent services to the State, to science, to industry and to education did not pass without recognition. He received the honour of knighthood in 1916. He was elected to the Royal Society in 1906 and was a member of the Council from 1917 to 1919 and a Vice-President in 1919. He also served as President of the Society of Chemical Industry (1898—1899), of the Institute of Chemistry (1909—1912), of the Institute of Metals (1916—1918), and of the Chemical Section of the British Association on the occasion of the meeting in South Africa in 1905. He received the Honorary Degrees of LL.D. from the Universities of Glasgow and Birmingham, and D.Sc. from the University of Durham.

Sir George Beilby was not only a leader of industry but above all a very zealous student of science from his early days in the University until failing health compelled his withdrawal from most of his activities, and his career bears eloquent testimony to the importance of scientific research to industry. One of the most modest and unassuming of men, his wide knowledge, well-balanced judgment, clearness of thought, and charm of manner made a deep impression upon all who came in contact with him in public and in private life. His integrity and directness rendered him impatient with anything that savoured of sham or pretence, but an earnest worker was always assured of his sympathy and encouragement. His generosity was inexhaustible, but, characteristically, was kept hidden except from very few. To all who worked with him his example will be an abiding inspiration. • G. G. H.

HENRY GEORGE SMITH.

BORN JULY 26TH, 1852; DIED SEPTEMBER 19TH, 1924.

HENRY GEORGE SMITH was born in 1852 at Littlebourne, in Kent, and he was educated at the neighbouring schools of Ickham and Wingham, and subsequently under the private tuition of the Rev. Mr. Midgley, M.A. Although possessing a decided bent for science, prior to his arrival in Australia for health reasons, in 1883, circumstances had prevented him from pursuing scientific studies. In the following year, however, he availed himself of an opportunity of joining the staff of the Sydney Technological Museum, then housed in the Domain, in a semi-scientific capacity. The next few years were utilised to the full by Smith in increasing his knowledge of science, particularly of chemistry; his efforts in this direction were warmly encouraged by the late Mr. W. A. Dixon, F.I.C., who was at the time lecturer in chemistry at the Sydney Technical College. Smith maintained a great interest in this institution, and from 1898 to 1911 he lectured to the evening classes at the College in organic chemistry.

In 1891, Smith was appointed laboratory assistant at the Technological Museum. The same year witnessed the publication of his first original paper, which appeared in the *Proceedings* of the Linnean Society of New South Wales, and announced the discovery of barytes in the Hawkesbury sandstones at Sydney. It is noteworthy that Smith was then thirty-nine years old. In 1895, he was appointed to the position of mineralogist at the Museum. By this time he had published five original papers, dealing with inorganic chemistry. In the same year appeared his first contribution to organic chemistry : a paper on eucalyptus kinos and the occurrence of eudesmin, published in collaboration with Mr. J. H. Maiden, in the *Proceedings* of the Royal Society of New South Wales. This paper was destined to assume peculiar significance, as the precursor of a long series of original publications dealing with the chemistry of the Australian flora. Smith's first original contribution to the chemistry of the Australian essential oils was carried out in collaboration with Mr. R. T. Baker, F.L.S. (late Curator and Economic Botanist of the Sydney Technological Museum), in 1897, the species concerned being the Sydney Peppermint (*Eucalyptus piperita*). The oil of this particular species had been distilled as far back as 1788 and used as a substitute for ordinary peppermint oil by Dr. White, Surgeon-General to the first settlement. In 1900, Smith was successful in isolating the substance giving rise to the characteristic odour; he showed it to be a ketone, $C_{10}H_{16}O$, and named it piperi-

tone. Many years later (J., 1924, **125**, 129) this ketone, the lævo-rotatory form of which has a wide distribution in the genus *Eucalyptus*, was shown to be chemically identical with Δ^1-*p*-menthen-3-one, synthesised by Wallach in 1908. Curiously, the dextrorotatory modification of this sole ketonic constituent of eucalyptus oils was identified in the essential oil of a Himalayan grass, *Andropogon Jwarancusa*, by Simonsen, during the progress of the later investigations of Smith and his collaborators (J., 1921, **119**, 1644).

In 1899, Smith was appointed Assistant Curator and Economic Chemist at the Museum, and his tenure of this post lasted until his retirement from the Government service in 1921; altogether he was associated with the Sydney Technological Museum for thirty-seven years. Most prominent among his record of accomplishment during this period stands the extensive series of researches into the chemical nature of the essential oils of the genus *Eucalyptus*. This work, which was conducted throughout in close collaboration with his botanical colleague, R. T. Baker, resulted in the establishment of a remarkable correlation between chemical and botanical characteristics in this complex genus, which includes some 250 distinct species. The examination of the essential oils of a numerous selection of species, representative of the Australian mainland and of Tasmania, revealed the presence of more than 40 distinct components; moreover, the oil from any particular species was found to show a remarkable constancy of composition; and each chemical constituent appeared to increase in amount through a certain range of species until it reached a maximum. A connexion was also traced between certain morphological characters, such as the type of the leaf venation, and the chemical nature of the corresponding oil: thus, a " feather " venation indicated the presence of pinene and possibly bornyl acetate; an intermediate venation was associated with the occurrence of pinene and cineole; and a " butterfly-wing " venation denoted phellandrene, and possibly piperitone or geranyl acetate.

A main outcome of these phyto-chemical researches, which included the detailed examination, not only of the essential oils, but also of the astringent exudations of more than 100 eucalyptus species, was the advancement by Baker and Smith of an evolutionary theory dealing with the chronological sequence in this genus and the older and related genus *Angophora*. The preliminary work, extending over a period of six years, was published in 1902, in a volume entitled " A Research on the Eucalypts, especially in regard to their Essential Oils." A revised edition of this *magnum opus* of Australian science, containing the results of a further eighteen years' observations, was published in 1920. The trend of

other investigations carried out by Smith, again largely in collabora-
tion with Baker, indicated that this fruitful idea of chemical and
botanical correlation is also destined to lead to valuable results in
other typical Australian genera. The work summarised in "A
Research on the Pines of Australia" (Sydney, 1910) may be referred
to as an example, and further investigations were directed towards
the melaleucas, leptospermums, boronias, and other widely distri-
buted groups. The two volumes on the Eucalypts and the Pines
of Australia are regarded as authoritative.

As typical results, not only of scientific interest, but also of direct
economic importance, may be mentioned the recognition of the many
rich cineole and phellandrene oils, and the discovery of oils yielding
unusually high proportions of such substances as geraniol (E.
Macarthuri, *Darwinia fascicularis*, *Callitris tasmanica*), citral
(*Leptospermum Liversidgei*), pinene (E. *dextropinea*, E. *lævopinea*),
and piperitone (E. *dives*). These examples illustrate the important
bearing of Smith's work on the development of the natural resources
of Australia. As examples of purely scientific interest, for the
present, may be mentioned the isolation of a series of constituents,
such as eudesmin, eudesmol, tasmanol, and gmelinol, which appear
to be peculiar to the Australian flora.

From about 1914 onwards, Smith became informally but actively
associated with the newly-founded Department of Organic Chemistry
at the University of Sydney, and upon his retirement from the
Technological Museum in 1920 he continued to work assiduously
at the University upon the chemical constitution and reactions of
piperitone, α-phellandrene, and other components of Australian
plant products, which had figured in his earlier work. The accounts
of these later investigations were published in the Chemical Society's
Journal (J., 1924, **125**, 129, 930; etc.); but the fact that his
sense of local patriotism and his modesty induced him to publish
the bulk of his work in Australia, rather than in Europe, undoubtedly
prevented his researches from attracting in full measure the general
attention which they so richly merited. Altogether, Smith published
well over 100 original contributions to chemical science, and of
these, 62 appeared in the *Proceedings* of the Royal Society of New
South Wales. The occasion of his retirement from the Sydney
Technological Museum, in 1921, in the general opinion of Austra-
lasian workers in science, offered a fitting opportunity for the award
to him of some higher form of recognition than he had hitherto
obtained for his eminent services to Australian science and Aus-
tralian economic development. It is pleasing to record that in the
following year he received the David Syme Prize of the University
of Melbourne, which is given for original scientific research connected

with the material and industrial development of Australia. The high esteem in which Smith was held among Australasian men of science is evidenced by his election to such offices as the Presidentships of the Royal Society of New South Wales (1913), the New South Wales branch of the Australian Chemical Institute (1922—1923), and the chemistry section of the Australasian Association for the Advancement of Science. In the last-named capacity he delivered his presidential address on the chemistry of the Australian flora at Wellington, New Zealand, in 1923. He was also an original member of the Australian National Research Council, and he conducted a good deal of valuable work under the auspices of the Commonwealth Institute of Science and Industry.

Smith died at Roseville, Sydney, on September 19th, 1924, at the age of seventy-two. He was twice married, and left a widow and family, including three sons. In all the relations of life quietly genial and considerate, Smith was distinguished by his modesty and sincerity. One of the most selfless of men, he achieved without seeking it a world-wide reputation; but his reward lay in his work and in his sure knowledge of the part it was destined to play in the economic development of his adopted and beloved land of Australia. Even after passing the three score years and ten, his natural ardour and activity for chemical investigation remained in full measure. To those of the younger generation of Australian chemists who were so fortunate as to be associated with him, his unfailing enthusiasm will act as a lasting inspiration. His practical knowledge of Australian natural products was profound. In the laboratory, his diagnosis of the chemical composition of an essential oil after a few rapid superficial tests was a revelation; in the bush, the tall trees were to him as familiar friends, and his intimate knowledge of their characteristics seemed at times to border upon wizardry. In spite of initial disabilities, including lack of preliminary training, and more lasting handicaps, such as complete isolation from any centre of organic chemical activity, and with less than could have been desired in the way of encouragement and material recompense, Smith devoted well over thirty years of incessant research to the elucidation of the chemical and economic significance of these products. To the last, he was an ardent, tireless worker, who regarded every hour in the spirit of the true man of science as a potential " bringer of new things "; to the last, he remained strong in will to bring the secrets of Nature into the service of man. His pioneering work is not only of high scientific and economic worth : it will remain to him a unique and enduring monument in the annals of Australian science. JOHN READ.

CXXVIII.—*Nitro- and Amino-ethoxylutidine.*

By JOHN NORMAN COLLIE and GERALD BISHOP.

PREVIOUS work on the nitro- and amino-lutidines (J., 1898, **73**, 229, 235) has been continued.

The ethoxylutidine (4-ethoxy-2 : 6-dimethylpyridine), b. p. 208°, was obtained from dimethylpyrone by treating it successively with ammonia, phosphorus pentachloride, and sodium ethoxide.

The *mononitroethoxylutidine* was prepared by dissolving the ethoxylutidine in strong sulphuric acid and adding a mixture of fuming nitric acid and sulphuric acid, the whole cooled in ice. After some time the mixture was poured into water, and neutralised with sodium carbonate. A bulky, white precipitate separated, m. p. 99°. The compound is slightly volatile with steam; it gives no colour with sodium hydroxide (Found : C = 54·8 ; H = 6·3 ; N = 14·5. $C_9H_{12}O_3N_2$ requires C = 55·1 ; H = 6·1 ; N = 14·3%).

Monoaminoethoxylutidine was prepared by reducing the nitro-compound with tin and hydrochloric acid. After the reaction a double tin salt crystallised out. It gave a light yellow precipitate with hydrogen sulphide [Found : Sn = 20·2 ; Cl = 34·9 ; H_2O = 1·5. $(C_9H_{14}ON_2,HCl)_3,2SnCl_4,H_2O$ requires Sn = 20·7 ; Cl = 34·1 ; H_2O = 1·5%].

The tin salt was treated with hydrogen sulphide, the filtrate evaporated to dryness, and extracted with ether. The platinum salt of the base comes down slowly, and once precipitated is very insoluble even in boiling water, or alcohol (Found : Pt = 35·9 ; Cl = 32·5 ; C = 20·0. $C_9H_{14}ON_2,HCl,PtCl_4$ requires Pt = 36·1 ; Cl = 32·8 ; C = 20·0%).

The above ethereal solution of the hydrochloride was made alkaline with sodium carbonate, and a small quantity of ammonia was evolved on evaporation. The concentrated solution was extracted with ether. On evaporation of the ethereal extract, an oil was obtained that slowly crystallised. The oil was soluble in cold water, but a concentrated solution became cloudy on warming, owing to separation of the base. The base, m. p. 62°, b. p. 267°, absorbs carbon dioxide, and is strongly alkaline. It gives a crystalline precipitate with silver nitrate, a white one with mercuric chloride, but none with lead acetate, and no colour with ferric chloride (Found : Ag = 28·0 ; H_2O = 8·7. $C_9H_{14}ON_2,AgNO_3,2H_2O$ requires Ag = 28·9 ; H_2O = 9·6%).

Oxidation of Mononitroethoxylutidine.—This compound was oxidised with a 1% solution of potassium permanganate. An acid was obtained that was easily recrystallised from hot water ; m. p.

147° (Found : N = 12·5. $C_9H_{10}O_5N_2$ requires N = 12·4%). The *silver* salt is anhydrous (Found : Ag = 32·5 ; C = 32·5 ; H = 3·4. $C_9H_9O_5N_2Ag$ requires Ag = 32·4 ; C = 32·4 ; H = 2·8%), and explodes faintly on heating. The sodium and ammonium salts are easily recrystallised from water. The copper, silver, mercury, iron, and calcium salts are insoluble in water.

Oxidation of Ethoxylutidine.—This compound was oxidised with a boiling 1% solution of potassium permanganate, containing enough permanganate to oxidise one only of the methyl groups. Some ethoxylutidine remained unoxidised. The resulting acid would only crystallise when the aqueous solution was evaporated to a syrup. It could not be purified sufficiently to give a satisfactory analysis and melted unsatisfactorily at 138°. The platinum salt was therefore made [Found : Pt = 28·4. $(C_9H_{11}O_3N,HCl)_2PtCl_4$ requires Pt = 23·9%]. The *silver* salt was precipitated (Found : Ag = 38·3. $C_9H_{10}O_3NAg$ requires Ag = 37·4%).

The syrupy impure acid was heated with fuming hydriodic acid, colourless crystals, m. p. 295°, being obtained (Found : C = 48·8 ; H = 5·5 ; H_2O = 8·8. $C_7H_7O_3N,H_2O$ requires C = 49·1 ; H = 5·3 ; H_2O = 10·5%). The substance is therefore 4-hydroxy-2-methylpyridine-6-carboxylic acid.

The syrupy acid heated alone gave carbon dioxide and an ethoxy-picoline, b. p. about 220°. The dried platinum salt, m. p. 207°, was analysed [Found : Pt = 28·4. $(C_8H_{11}ON,HCl)_2PtCl_4$ requires Pt = 28·5%].

The acid on further oxidation with permanganate was entirely decomposed. Nitric acid on boiling and then evaporating gave a crystalline *nitrate*, m. p. 125°, which gave the ordinary tests for a nitrate (Found : N = 11·4. $C_9H_{11}O_3N,HNO_3$ requires N = 11·5%). When the ethoxylutidine was oxidised with a slight excess of potassium permanganate over that required to oxidise both methyl groups, the product contained a mixture of the mono- and di-basic acids. An acid, m. p. 200°, was finally separated (Found : C = 51·5 ; H = 4·8 ; *M*, by titration with N/10-sodium hydroxide, = 210. $C_9H_9O_5N$ requires C = 51·2 ; H = 4·3% ; *M* = 211). *Silver* salt (Found : Ag = 50·6. $C_9H_7O_5NAg_2$ requires Ag = 50·8%). *Platinum* salt (Found : Pt = 23·6. Theory requires Pt = 23·4%).

The syrupy residue from which the acid, m. p. 200°, had been separated gave carbon dioxide when heated, and on distillation a fraction, b. p. 350—360°, was obtained that solidified on cooling. It was made into the platinum salt [Found : Pt = 30·2 ; H_2O = 2·4. $(C_6H_7ON,HCl)_2PtCl_4,H_2O$ requires Pt = 30·2 ; H_2O = 2·8%]. The substance is therefore 4-hydroxy-2-methylpyridine, and has been formed by the ethyl group being oxidised by the permanganate.

The acid, m. p. 200°, when distilled, gave carbon dioxide and an oil, b. p. 200—202°. Its platinum salt melted at 215° [Found : $Pt = 28.9$; $H_2O = 2.5$. $(C_7H_9ON,HCl)_2PtCl_4$ requires $Pt = 28.9$; $H_2O = 2.6\%$]. The compound therefore is 4-ethoxypyridine.

THE RALPH FORSTER LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON.   [Received, February 19th, 1925.]

CXXIX.—Reactions of Triethylphosphine.

By JOHN NORMAN COLLIE.

THE triethylphosphine was made by Hofmann's method of adding phosphorus trichloride to an ethereal solution of zinc ethyl. After adding the sodium hydroxide and distilling off the triethylphosphine, more solid sodium hydroxide was added; an oil separated which, on boiling, dissolved with evolution of hydrogen. The residue was made acid with hydrochloric acid, evaporated to dryness, and extracted with alcohol. From the alcoholic extract diethyl-phosphinic acid was obtained. $PCl_3 + ZnEt_2 = ZnCl_2 + PEt_2Cl \longrightarrow PEt_2 \cdot OH \longrightarrow PEt_2O \cdot OH$. This acid boiled at about 320° without decomposition. It solidified in a freezing mixture to a mass of long needles radiating from a centre. Boiled with silver hydroxide, it gave a soluble silver salt which was stable and not decomposed by boiling. After evaporation, the concentrated solution was precipitated with alcohol, the silver salt coming down in long, anhydrous, silky needles (Found : $Ag = 46.6$, 46.1. Calc. for $C_4H_{10}O_2PAg$, $Ag = 47.0 \%$).

The reaction of triethylphosphine with chlorides of the non-metals is quite anomalous. If added to either phosphorus trichloride or phosphorus oxychloride, it reacts with great violence with the formation of free phosphorus. If the oxychloride be dissolved in dry ether, triethylphosphine gives a white precipitate, but this compound soon decomposes, yielding yellow phosphorus. Silicon tetrachloride and sulphur monochloride react in an exactly similar manner, silicon and sulphur being produced. It is curious that metallic chlorides do not behave in the same way. Tin tetrachloride does not react at all violently and gives a white double salt. Zinc chloride behaves also in the same manner; whilst some halogen derivatives of hydrocarbons will not react at all. Chloro- and bromo-benzene may be boiled with triethylphosphine, or left for weeks with it without any reaction. Iodobenzene reacts very slowly, and four-sided plates are produced [Found : $I = 39.8$. $P(C_2H_5)_3(C_6H_5I)$ requires $I = 39.4 \%$]. Trimethylene dibromide also reacts very

slowly, small, white crystals being deposited [Found : Br = 24·8. $P(C_2H_5)_3(CH_2)_3Br_2$ requires for one bromine atom, Br = 25·0 %].

Aldehydes also react with triethylphosphine. With chloral there is a powerful reaction, the chief product being metachloral, in fact if a trace only of triethylphosphine be added to chloral, after a short time the whole becomes nearly solid. When triethylphosphine is added to a solution of chloral hydrate in dry ether, an oil separates which is soluble in water and gives a chloroplatinate (Found : Pt = 21·3. $[P(C_2H_5)_3C_2H_3Cl_3O_2]_2PtCl_4$ requires Pt = 21·5 %).

When a solution of formalin is shaken with triethylphosphine, the latter dissolves, the mixture becomes warm, and all smell of the phosphine disappears, also the solution becomes alkaline, owing to the formation of the quaternary phosphonium hydroxide. On the addition of hydrochloric acid and platinum tetrachloride a crystalline salt is obtained (Found : Pt = 27·4. $[P(C_2H_5)_3CH_3OCl]_2PtCl_4$ requires Pt = 27·6 %).

A similar compound is obtained with acetaldehyde (Found : Pt = 26·5. $[P(C_2H_5)_3C_2H_5OCl]_2PtCl_4$ requires Pt = 26·6 %).

THE RALPH FORSTER LABORATORY OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 19th*, 1925.]

CXXX.—*Derivatives of Semioxamazide.* Part III.

By FORSYTH JAMES WILSON and ERIC CHARLES PICKERING.

IN this communication the action of heat on ketonic semioxamazones is described. From acetophenonesemioxamazone (I) the products were phenylmethylketazine, a little *acetophenoneoxalyldihydrazone* (II), and a mixture of oxamide and *cyclo*oxalylhydrazide. This would indicate that the decomposition of the semioxamazone by heat takes place in two stages—

$$NH_2 \cdot CO \cdot CO \cdot NH \cdot N{:}CMePh \atop NH_2 \cdot CO \cdot CO \cdot NH \cdot N{:}CMePh \quad = \quad {NH_2 \cdot CO \atop NH_2 \cdot CO} \quad + \quad {CO \cdot NH \cdot N{:}CMePh \atop CO \cdot NH \cdot N{:}CMePh}$$

$$\text{(I.)} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(II.)}$$

$$\rightarrow \quad {CO\text{—}NH \atop CO\text{—}NH} \quad + \quad {N{:}CMePh \atop N{:}CMePh}$$
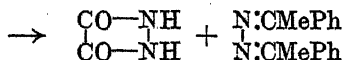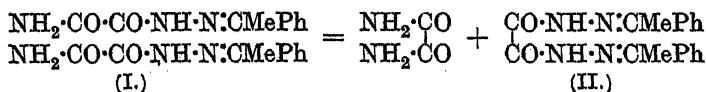
This explanation was confirmed by investigation of the products obtained by heating ethyl acetoacetate semioxamazone (III) at its melting point for several hours. The products isolated were oxamide, *cyclo*oxalylhydrazide, and a substance, m. p. 247°, which proved to be 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone (IV), investigated by Bülow and Lobeck (*Ber.*, 1907, **40**, 708), Bülow and Schaub (*ibid.*, 1908, **41**, 1945) and by Wolff and Schreiner (*ibid.*, 1908, **41**, 550).

These authors showed that ethyl oxalylbishydrazoneacetoacetate (V) on heating gives *cyclo*oxalylhydrazide and (IV)—

(V.) $\begin{array}{l}\text{CMe:N·NH·CO·CO·NH·N:CMe}\\ \text{CH}_2\text{·CO}_2\text{Et} \qquad\qquad\qquad \text{CH}_2\text{·CO}_2\text{Et}\end{array}$ $=\ \begin{array}{l}\text{CO——CO}\\ \text{NH——NH}\end{array}\ +$

$\begin{array}{l}\text{CMe:N—N=CMe}\\ \text{CH}_2\text{·CO}_2\text{Et}\quad\text{CH}_2\text{·CO}_2\text{Et}\end{array}\ \longrightarrow$

$+$ 2EtOH. (IV.)
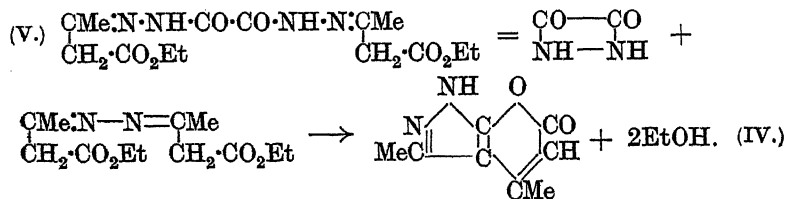
In the case under discussion, (V) would be formed, together with oxamide, from the semioxamazone—

$\begin{array}{l}\text{CMe:N·NH·CO·CO·NH}_2\\ \text{CH}_2\text{·CO}_2\text{Et}\quad\text{(III.)}\end{array}\ +\ \begin{array}{l}\text{NH}_2\text{·CO·CO·NH·N:CMe}\\ \qquad\qquad\qquad\text{CH}_2\text{·CO}_2\text{Et}\end{array}\ =$

$\text{C}_2\text{O}_2(\text{NH}_2)_2\ +\ \text{(V.)}$
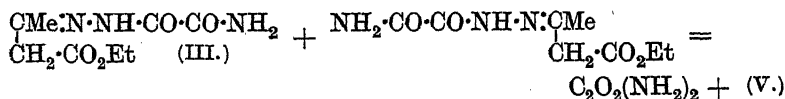
The action of heat on the semioxamazones of dibenzyl ketone, acetone, and methyl ethyl ketone was also investigated, the products being the corresponding ketazine, oxamide, and *cyclo*oxalylhydrazide; the intermediate oxalyldihydrazones were not isolated in these cases.

EXPERIMENTAL.

Acetophenonesemioxamazone.—This substance was heated at 215° for 4 hours. The semi-solid mass when cold was powdered and treated with ether, which dissolved phenylmethylketazine; the insoluble residue was repeatedly extracted with boiling absolute alcohol. On cooling, a small quantity of oxamide was deposited from the extract, followed by *acetophenoneoxalyldihydrazone* (described below); concentration of the mother-liquors gave unchanged semioxamazone only.

A portion of the residue left after the alcohol extraction was boiled with sodium hydroxide solution, ammonia being evolved. The residual solution reduced silver nitrate in the cold, indicating the presence of hydrazine, and contained oxalic acid. Another portion was warmed with ammonia solution, in which it was partly soluble; the residue gave ammonia and an oxalate on heating with sodium hydroxide. The ammoniacal solution was made just acid with nitric acid, the white precipitate after filtration was redissolved in ammonia, and silver nitrate added to the solution, neutralised with nitric acid, when the yellow silver derivative of *cyclo*oxalylhydrazide was deposited. These facts indicate that the insoluble product was a mixture of oxamide and *cyclo*oxalylhydrazide (Found : N = 32·9, 31·9. Calc., for oxamide, N = 31·8; for *cyclo*oxalylhydrazide, N = 32·5%).

Acetophenoneoxalyldihydrazone, which has not previously been prepared, was obtained as a crystalline precipitate by boiling

acetophenone and oxalyldihydrazide (mol. quantities) in absolute alcohol with a little iodine, without which no perceptible reaction took place; it separated from alcohol in needles, m. p. 250° (Found: N = 17·0. $C_{18}H_{18}O_2N_4$ requires N = 17·4%).

Ethyl acetoacetate semioxamazone.—The substance was heated at 130–135° for 2 hours, and the semi-solid mass when cold was extracted with boiling absolute alcohol. The insoluble residue was identified in the usual way as a mixture of oxamide and *cyclo*-oxalylhydrazide. The alcoholic solution on concentration deposited a substance which after recrystallisation from the same solvent formed prismatic needles, m. p. 247°, and was identified as 3 : 4-di-methyl-1 : 2-pyrazo-6 : 7-pyrone by analysis (Found : N = 17·30, 17·14. Calc., N = 17·07%) and by comparison with an authentic specimen. Further concentration of the alcoholic extract gave unaltered semioxamazone.

Dibenzyl ketone semioxamazone.—On heating at 200° for 2 hours a little ammonia was evolved and a white sublimate produced. The product was extracted with ether and alcohol successively. The ethereal extract gave dibenzylketazine (m. p. 95—96°); the alcoholic extract contained unaltered substance only. The insoluble residue consisted of oxamide and *cyclo*oxalylhydrazide.

Acetonesemioxamazone.—The dry substance was heated at 180° in a distillation flask arranged as for a vacuum distillation; in 4 hours a small quantity of liquid had distilled over, and more on reducing the pressure slightly. The liquid was dimethylketazine; the residue in the flask, a mixture of oxamide and *cyclo*oxalylhydrazide.

Methyl Ethyl Ketone Semioxamazone.—The reaction was carried out exactly as in the previous case, the products being methyl-ethylketazine, oxamide, and *cyclo*oxalylhydrazide.

In conclusion, we desire to thank the Carnegie Trust for the Universities of Scotland for a grant which has partly defrayed the expenses of this work.

THE ROYAL TECHNICAL COLLEGE,
　　GLASGOW.　　　　　　　　　　[*Received, February 21st, 1925.*]

CXXXI.—*Colour and Molecular Geometry. Part III. A Graphical Presentation of the Theory.*

By JAMES MOIR.

THE author's theory of colour is handicapped by the fact that it has a mathematical basis of some complexity, more readily comprehensible by an astronomer than by an organic chemist. He

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has therefore presented, by means of a graph, some of the results of the theory.

Even when the hapton * is a derivative of carbon or sulphur, it would appear that in most cases it is the nitrogen or oxygen contained in the hapton that is the active part, *i.e.*, constitutes the second positive centre. A great simplification then arises from the fact that the nitrogen and oxygen atoms have the same size (1·3 Å.) and occur at both ends of the molecule.

FIG. 1.

Value of 2x, the distance between the two positive centres : tenth metre units.

Calculated position (λ) of absorption bands.   Unit μμ or 10⁻⁷ cm.
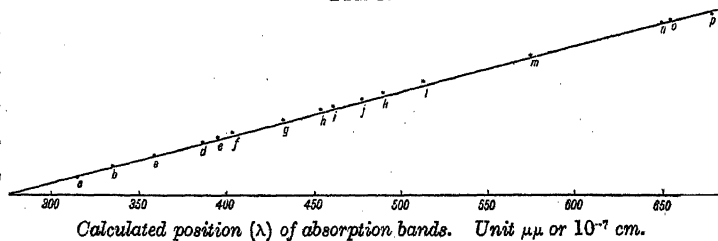
References.

a = *Quinol, p-aminophenol, and p-phenylenediamine.*
b = *p-Diketohexamethylene (also free quinonephenylhydrazone).*
c = *Quinoneimine.*
d = *p-Hydroxyazobenzene ion (lower band in alkali).*
e = *p-Nitrophenol* ⎫ *(alkaline).*
f = *p-Nitrosophenol* ⎭
g = *p-Hydroxyazobenzene ion (upper band in alkali).*
h = *Quinone : also p-nitrophenylhydrazine in alkali.*
i = *Lower band of acidified p-hydroxyazobenzene.*
j = *Lower band of acidified aminoazobenzene.*
k = *Upper band of acidified p-hydroxyazobenzene.*
l = *Dihydroxyphenazine, diaminophenazine, upper band of acidified aminoazo-benzene, azophenol and azoaniline.*
m = *Resorufin.*
n = *Indophenol.*
o = *Indamine.*
p = *Quinhydrone.*

In addition, *dihydroxy- and diamino-diphenyl sulphoxide, with λ about 750, fall on the same line with small deviation due to the slightly larger size of the sulphur atom.*

The author's equation

$$\lambda = 112\, a^{3/2} f(e) \quad . \quad . \quad . \quad . \quad . \quad \text{(I)}$$

then becomes [since a is now $(c + 0.65)$, and $f(e) = 1.249 - 0.79c/a$ †

$$\lambda = 51.4\, (c + 1.77)\sqrt{c + 0.65} \quad . \quad . \quad . \quad \text{(II)}$$

in which c is half the distance between two positive centres round which the electron moves (two different oxygen or nitrogen atoms). The colour thus depends solely on this distance c.

* For definitions see J., 1923, **123**, 2801.
† See J., 1924, **125**, 1137, 1138.

The graph of this equation over the range of the visible spectrum is practically a straight line. It is shown in Fig. 1 by a series of dots; a straight line is drawn for comparison through the top and bottom results. Each dot corresponds to a coloured substance of which the auxochrome is either –OH or –NH$_2$, and of which the active part of the hapton is oxygen or nitrogen or both.

This approximate proportionality of height of colour (λ) to interfocal distance ($2c$) renders calculation of colour easy. The following table contains some of the data from the graph.

| 2c (in Å).* | λ (in $\mu\mu$). | | 2c (in Å).* | λ (in $\mu\mu$). | |
	a. New equation (II).	b. Old equation (I).		a. New equation (II).	b. Old equation (I).
1·3	142	138	6·0	469	469
2·6	220	218	6·5	510	509
3·9	308	308	7·0	552	550
4·5	352	352	7·5	595	596
5·0	390	390	8·0	640	641
5·5	429	429			

* Contact of the two positive atoms (oxygen or nitrogen).

It would follow that no absorption band lower than λ 138 is possible. Diagrams which are at least plausible have been drawn representing exactly to scale the configurations of all the substances mentioned in Fig. 1. Each diagram has the correct interfocal distance required to give the observed absorption band and, in the author's opinion, represents the real shape and arrangement of the molecules. Physicists may perhaps be astonished at the organic chemist's conception of molecules of such rigid structure; and some organic chemists may be astonished at the conception that the function of the benzene ring in coloured substances is to provide rigidity (and not unsaturation); but the evidence for both conceptions is satisfactory.

Fig. 2 represents ionised quinol, or p-phenylenediamine or p-aminophenol. The distance between the positive centres ($2c$) is 4·00 Å., corresponding to λ about 315, which is actually possessed by all three substances (as would be expected if oxygen and nitrogen have the same atomic diameter).

Fig. 3 represents p-benzoquinone as a flat hexagon with a very slight overlap of the middle carbon atoms at the double bonds. The distance between the oxygen centres is about 5·88 Å., exactly what is required to account for its band at about λ 455.

Fig. 4 represents p-diketohexamethylene (*cyclo*hexanedione) as a compromise between the flat hexagon and the skew-hexagon of Bragg. The value of $2c$ is about 4·2 Å. and the absorption band (in presence of alkali) is at λ 335.

L L* 2

Fig. 5 represents *p*-benzoquinoneimine seen sideways. The circle marked X is the hollow centre of the flat benzene ring of quinone (which is of the same size as a carbon atom). The –NH group lies nearly at right angles to the ring. The distance ON ($2c$) is about 4·6 Å., corresponding to λ 365 observed.

Fig. 6 represents two phases of *p*-nitrosophenol (in alkali) in which the oxygen of the nitroso-group can occupy two positions symmetrical about the line of the benzene valency. If the deviation is 45°, the distances O'O" and O'O are about 3·8 and 5·2 Å., each of which corresponds to an absorption band (observed λλ about 400 and 270).

Fig. 7 represents the skeleton of the parent-substance of *p*-hydroxyazobenzene, $NH\colon N\cdot C_6H_4\cdot OH$, and is referred to later.

Fig. 8 represents *p*-nitrophenol (in alkali). This, like nitrosophenol, has two bands, λλ about 390 and 238, both of which are correctly predictable from the diagram. The oxygens of the nitro-groups are at right angles to the benzene valency.

Fig. 9 represents *p*-nitrophenylhydrazine (activated by alcoholic potash). The distance between O' and the farthest N agrees with the absorption band described in Part II of this series.

Fig. 10 represents potassium *p*-nitrophenyldiazotate,

$$NO_2\cdot C_6H_4\cdot N(OK)\colon N \text{ or } NO_2\cdot C_6H_4\cdot N\colon N\cdot OK,$$
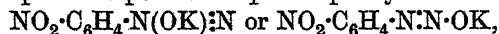
a substance which is colourless. The small distance between the oxygens of the active groups is a plausible explanation (see addendum to Part II).

Fig. 11 represents the ordinary configuration of *p*-hydroxyazobenzene (in alkali). The distance 5·3 Å. between O' and N corresponds by calculation to λ 412. This is raised to λ 433 (observed for the *upper* alkali band) by the "loading" of the (inactive) phenyl group. Fig. 12 gives the arrangement for the *lower* alkali band of the same substance ($2c = 4\cdot 87$ Å., λ about 390).

Fig. 13 gives the probable arrangement for this substance without alkali, when it is very pale and is not ionised. The value of $2c$ is 3·8 Å. Fig. 13A is an azomethine. The colour is lower because the N lies at 125° to carbon as in the hydroxybenzaldehyde.

Fig. 14 attempts to explain both bands of *acidified* *p*-hydroxyazobenzene by representing the active ring as flattened out as in quinone. The distances $ON_{\prime}$ and $ON_{\prime\prime}$ are in agreement with the requirements. The same diagram serves for acid *p*-aminoazobenzene, which has two bands slightly higher than those of *p*-hydroxyazobenzene. A very slight rotation of $N_{\prime\prime}$ relatively to $N_{\prime}$ is required. The quinonoid configuration $NH\colon C_6H_4\colon N\cdot NHPh$ is assumed to exist when the ring is flat.

Fig. 15 represents Chattaway and Clemo's substances (J., 1923,
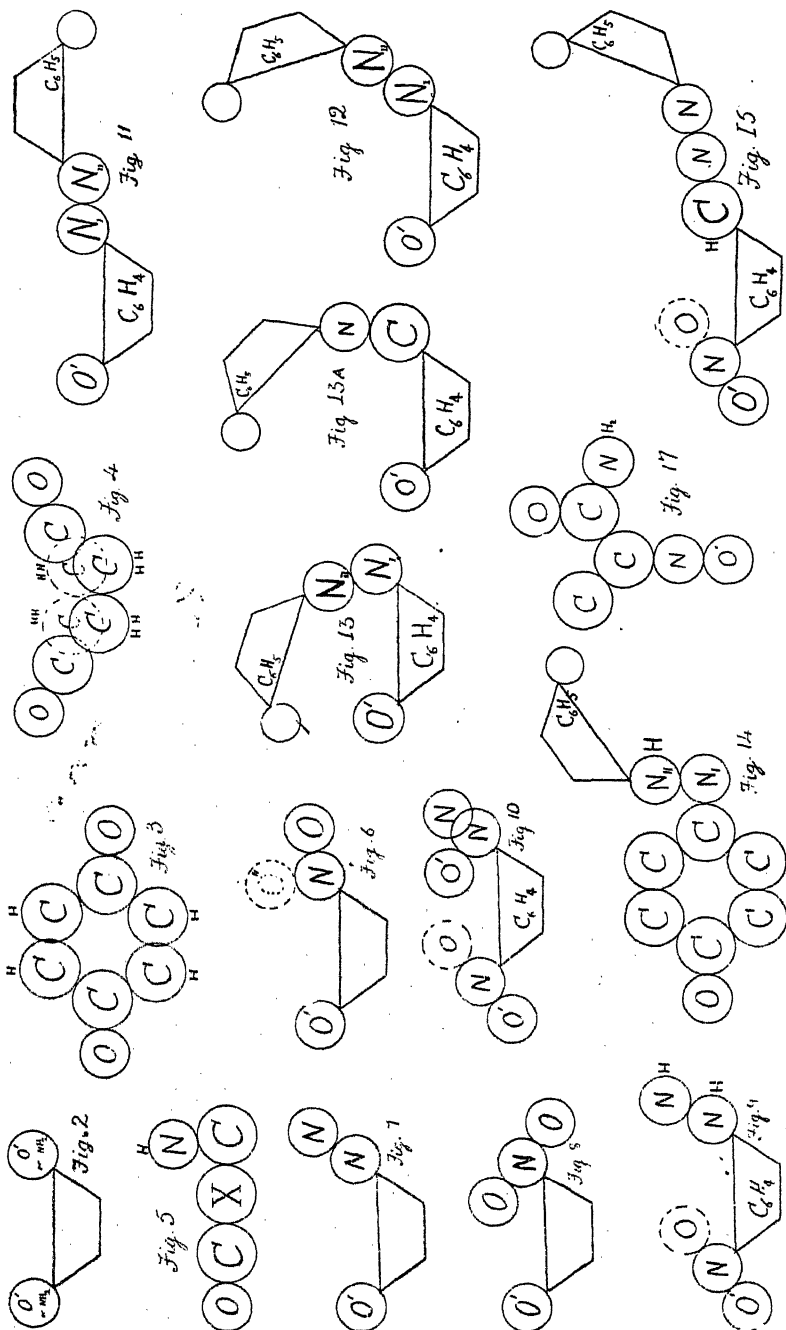
123, 3041), the one of highest colour (*p*-nitrobenzaldehydephenyl-hydrazone) being chosen for this purpose. The distance from O' to the more remote N is in agreement with the theory.

Fig. 16 represents the configuration of the ion of the violurates, the distance from O' to the most distant O agreeing with the observed colour (λ 570 when perfectly neutral, rather lower when faintly alkaline). Fig. 17 similarly gives the essential part of the molecule of Whiteley's *iso*nitrosomalonamide (which is yellow when alkaline), a substance obviously connected with the problem of the colour of the violurates.
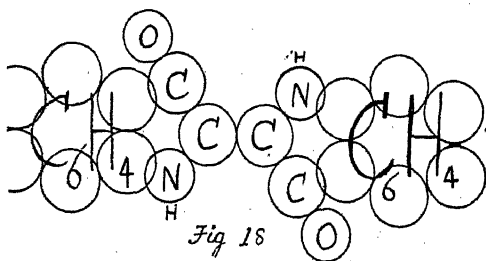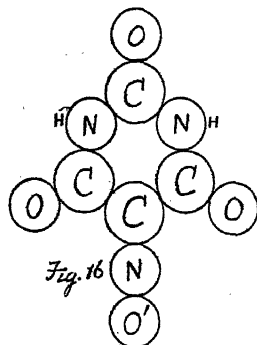
Fig. 18 represents indigotin. The distance between the two oxygen atoms corresponds to λ about 550. The observed position of the band is λ about 600, and the difference is due to the very oblique position of the two phenylene groups, which is capable (on other evidence) of giving a "loading" of 10%. The view of the C_6H_4 groups is that of the Bragg configuration seen from above.

The configurations of the other substances mentioned in Fig. 1 (such as resorufin) cannot be adequately represented by plane drawings, but agree with the theory.

It is probable that the performance of an orbit by an electron round two positive centres is not only the cause of colour but is the explanation of Lapworth's α—γ tautomerism and of other "balanced" actions. Baly's "isorropesis" is a glimpse of this idea written in pre-electronic days, just as Thiele's "partial valencies" was a prophecy of the linking of two atoms by three electrons.

CXXXII.—*Studies in the Benzothiazole Series. Part III. The Pseudo-bases of the 1-Substituted Benzothiazole Quaternary Salts.*

By LESLIE MARSHALL CLARK.

THE work of Mills, Clark, and Aeschlimann (J., 1923, **123**, 2353) on the ψ-bases produced by the action of alkalis on the quaternary salts of benzothiazole has now been extended to the quaternary salts of 1-substituted benzothiazoles.

As was to be expected from the previous results, the ψ-bases are substituted thiophenols which are readily oxidised with iodine or atmospheric oxygen to the corresponding disulphides : the identity of these disulphides has been established by direct acylation of 2 : 2'-dimethylaminodiphenyl disulphide with the appropriate acid chloride or anhydride.

The reaction is expressed by the following scheme, R being the substituent radical :

$$C_6H_4 \underset{NMeI}{\overset{S-}{<}} \hspace{-6pt}> CR \xrightarrow{NaOH} C_6H_4 \underset{NMe\cdot COR}{\overset{SH}{<}} \xrightarrow{O} \left[C_6H_4 \underset{NMe\cdot COR}{\overset{S-}{<}} \right]_2$$

The action of formic acid on bis-2-methylbenzothiazoline-1 : 1-spiran (I) confirms the formula assigned to this compound by Mills, Clark, and Aeschlimann (J., 1923, **123**, 2365). When the spiran is boiled with 90% formic acid, 2-methylbenzothiazolone (II) can be isolated from the reaction mixture after partial neutralisation with ammonia. The remaining solution still contains benzothiazole methoformate, since, by making it alkaline with ammonia and exposing to atmospheric oxidation, 2 : 2'-diformylmethylamino-diphenyl disulphide is obtained. This behaviour is characteristic of benzothiazolonium salts (Mills, Clark, and Aeschlimann, *loc. cit.*). Bis-2-methylbenzothiazoline-1 : 1-spiran is therefore hydro-lysed by formic acid thus :

$$C_6H_4 \underset{NMe}{\overset{S-}{<}} \hspace{-6pt}> C \underset{NMe}{\overset{S-}{<}} \hspace{-6pt}> C_6H_4 \xrightarrow{H_2O}$$

(I.)

$$C_6H_4 \underset{NMe}{\overset{S-}{<}} \hspace{-6pt}> CO + C_6H_4 \underset{NHMe}{\overset{SH}{<}}$$

(II.)   (III.)
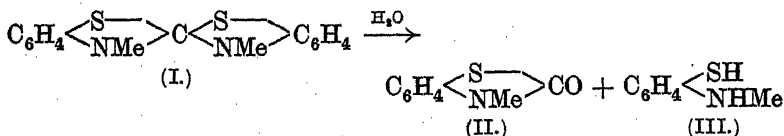
o-Methylaminophenyl mercaptan (III), which is presumably the second hydrolysis product, is formylated during the reaction to give benzothiazole methoformate (V) by way of the intermediate ψ-base (IV) :

$$(III.) \longrightarrow C_6H_4 \underset{NMe\cdot CHO}{\overset{SH}{<}} \longrightarrow C_6H_4 \underset{\overset{N}{\underset{\overset{\wedge}{Me}}{}}}{\overset{S}{<}} \hspace{-6pt}> CH \quad (V.)$$

(IV.) $\overset{\wedge}{Me}$ HCO_2
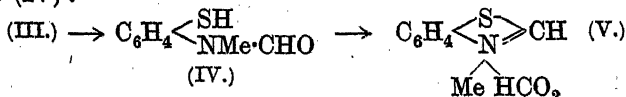
EXPERIMENTAL.

Atmospheric Oxidation of the ψ-Bases.—An aqueous solution of the alkyliodide and 10% ammonia was kept in the dark for 6—8 weeks, when the crystalline deposit was collected.

1-Methylbenzothiazole methiodide (Mills, J., 1922, **121**, 455) (1 g.; water, 10 c.c.; 10% ammonia, 4 c.c.; time, 6 weeks) gave 2 : 2′-*diacetylmethylaminodiphenyl disulphide*, which crystallised from aqueous alcohol in colourless needles (Found: C, 60·1; H, 5·6; N, 7·6. $C_{18}H_{20}O_2N_2S_2$ requires C, 60·0; H, 5·55; N, 7·8%). The same compound was prepared by boiling 2 : 2′-dimethylamino-diphenyl disulphide (Harries and Lowenstein, *Ber.*, 1894, **27**, 867) (0·3 g.) for 5 minutes with acetic anhydride, decomposing the excess of anhydride with water, and crystallising the product from aqueous alcohol (Found: N, 7·9%). Both specimens melted at 171°, alone or mixed.

From 1-methylbenzothiazole ethiodide (3 g.; 10% ammonia, 6 c.c.; time, 2 months) 2 : 2′-*diacetylethylaminodiphenyl disulphide* was obtained which crystallised from light petroleum in colourless needles, m. p. 103° (Found: C, 61·5; H, 6·3; N, 7·25. $C_{20}H_{24}O_2N_2S_2$ requires C, 61·8; H, 6·2; N, 7·2%).

1 : 5-Dimethylbenzothiazole ethiodide (Mills, *loc. cit.*) (1 g.; 10% ammonia, 4 c.c.; time, 2 months) gave 2 : 2′-*diacetylethyl-amino-5 : 5′-dimethyldiphenyl disulphide*, which crystallised from light petroleum in colourless needles, m. p. 129° (Found: C, 63·6; H, 6·8; N, 6·55. $C_{22}H_{28}O_2N_2S_2$ requires C, 63·5; H, 6·7; N, 6·7%).

Titration of 1-Methylbenzothiazole Ethiodide with Sodium Hydroxide. —When an aqueous solution of the salt is titrated with sodium hydroxide and phenolphthalein, the red colour of the indicator persists for some seconds after each fresh addition of the alkali, finally fading as the sodium salt of the thiophenol is formed. This time interval becomes so prolonged when nearly the two equivalents of alkali required by theory have been added that a sharp end-point cannot be obtained. 0·2703 G. of the salt required 17·2 c.c. of 0·1N-NaOH. Calc., 17·65 c.c.

1-*Phenylbenzothiazole Methiodide.*—1-Phenylbenzothiazole (pre-pared by heating together a mixture of benzanilide and sulphur) (1·6 g.) was heated with methyl iodide (1·5 g.) at 100° for 24 hours: the solid product, after extraction with ether to remove unchanged base, crystallised from alcohol in yellow plates, m. p. 218° (decomp.) (Found: I, 36·3. $C_{14}H_9NIS$ requires I, 36·3%).

Oxidation of the ψ-Base of 1-Phenylbenzothiazole Methiodide with Iodine.—The clear solution obtained from the salt (1·5 g.) and 10% sodium hydroxide (5 c.c.) in water (600 c.c.) was treated slowly

with a solution containing 0·7 g. of iodine. The white precipitate of 2 : 2′-*dibenzoylmethylaminodiphenyl disulphide* crystallised from aqueous alcohol in colourless plates (Found : C, 69·75; H, 5·0; N, 5·8. $C_{28}H_{24}O_2N_2S_2$ requires C, 69·4; H, 5·0; N, 5·8%). The same compound was obtained from 2 : 2′-dimethylaminodiphenyl disulphide, benzoyl chloride, and sodium hydroxide solution. Both specimens melted at 164°, alone or mixed.

Hydrolysis of Bis-2-methylbenzothiazoline-1 : 1-spiran.—The spiran (0·5 g.) was boiled gently for 4½ hours with 90% formic acid (5 c.c.), the solution poured into water and partly neutralised with ammonia, whereby a colourless oil, which eventually solidified, was thrown out. This substance crystallised from light petroleum in clusters of plates. It melted at 76°, alone or mixed with authentic 2-methyl-benzothiazolone (m. p. 76°).

The aqueous filtrate was made alkaline with ammonia and kept in the dark for 2 days. The yellow film of solid which had separated was washed, dried, and extracted with light petroleum, in which it was very sparingly soluble. The extracts, on rubbing, slowly deposited small, colourless plates of 2 : 2′-diformylmethylamino-diphenyl disulphide; these melted at 106—107·5°, alone or mixed with an authentic specimen of the disulphide.

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      CAMBRIDGE.   [*Received, February 25th*, 1925.]

CXXXIII.—*The Compounds Formed by the Action of Bromine upon Benzaldehydephenylhydrazone.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

THE bromination of benzaldehydephenylhydrazone was first studied by Ciusa and Vecchiotti (*Gazzetta*, 1916, 46, i, 240).

From the product obtained when 3 mols. of bromine were added to 1 mol. of the hydrazone in acetic acid solution, they isolated a tribromo-derivative, m. p. 114°.

They obtained the same compound by the bromination of the corresponding 2 : 4-dibromophenylhydrazone, and showed that it was not benzaldehyde-2 : 4 : 6-tribromophenylhydrazone, which they prepared from benzaldehyde and 2 : 4 : 6-tribromophenyl-hydrazine. Since by oxidation of the compound they obtained

p-bromobenzoic acid, they assigned to it the constitution of p-bromo-benzaldehyde-2 : 4-dibromophenylhydrazone (I).

Humphries, Bloom, and Evans (J., 1923, **123**, 1771) have described the same tribromo-derivative, m. p. 114°, and, without referring to the formula previously given by Ciusa and Vecchiotti, regard it as having the structure (II), on the ground that benzophenone-2 : 4-dibromophenylhydrazone is not further brominated under similar conditions.

In the course of an investigation of phenylhydrazones, the action of bromine on benzaldehydephenylhydrazone has been studied, and the constitution of the above product definitely settled in favour of the second alternative, namely, ω-bromobenzaldehyde-2 : 4-di-bromophenylhydrazone, since the same compound is obtained by the action of phosphorus pentabromide upon β-benzoyl-2 : 4-di-bromophenylhydrazine :
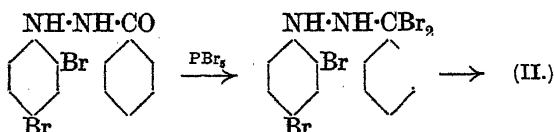
The constitution suggested by Ciusa and Vecchiotti has been disproved by the direct preparation of p-bromobenzaldehyde-2 : 4-dibromophenylhydrazone from p-bromobenzaldehyde and 2 : 4-dibromophenylhydrazine. It is a colourless compound, melting at 126°, and quite distinct in appearance and properties from that obtained by the bromination of benzaldehydephenylhydrazone. The formation of p-bromobenzoic acid observed by Ciusa and Vecchiotti must therefore be attributed to the action of bromine liberated during the oxidation.

When boiled for a short time with acetic acid and sodium acetate, ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone is changed almost quantitatively into α-acetyl-β-benzoyl-2 : 4-dibromophenyl-hydrazine, which yields on hydrolysis acetic acid, benzoic acid, and 2 : 4-dibromophenylhydrazine. The formation of this hydrazide may be represented as an acetylation of the imino-group, and replacement of the methine bromine by hydroxyl :

(II.) $\xrightarrow{\text{C}_2\text{H}_4\text{O}_2}$ $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NAc}\cdot\text{N:CBrPh}$ $\xrightarrow{\text{H}_2\text{O}}$

$\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NAc}\cdot\text{N:C(OH)Ph}$ $\longrightarrow$ $\text{C}_6\text{H}_3\text{Br}_2\cdot\text{NAc}\cdot\text{NH}\cdot\text{COPh}$.
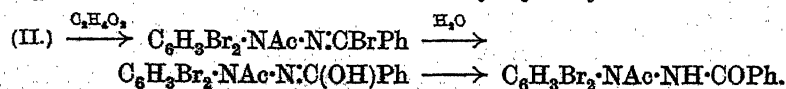
Its structure is further confirmed by its synthesis from 2 : 4-di-bromophenylhydrazine, by benzoylation, followed by acetylation of the product.

The ω-bromine in ω-bromobenzaldehyde-2 : 4-dibromophenyl-hydrazone shows the usual reactivity of halogen in benzal compounds.

For example, it reacts readily with ammonia in alcoholic solution to form a hydrazidine, the bromine being replaced by an amino-group :

$$C_6H_3Br_2 \cdot NH \cdot N{:}CPhBr \longrightarrow C_6H_3Br_2 \cdot NH \cdot N{:}CPh \cdot NH_2.$$
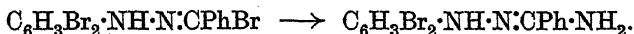
When warmed with potassium cyanide in aqueous-alcoholic solution, this bromine is replaced by a cyano-group in a similar manner.

Like ω-chlorobenzaldehydephenylhydrazone, NHPh·N:CPhCl (Pechmann, *Ber.*, 1894, **27**, 322), ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone reacts with phenylhydrazine to give a brightly coloured formazyl derivative :

$$C_6H_3Br_2 \cdot NH \cdot N{:}CPhBr \longrightarrow [C_6H_3Br_2 \cdot NH \cdot N{:}CPh \cdot NH \cdot NHPh] \longrightarrow$$
$$C_6H_3Br_2 \cdot NH \cdot N{:}CPh \cdot N{:}NPh.$$
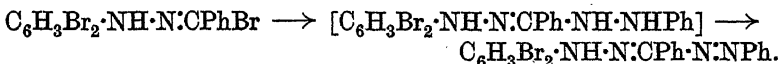
The bright red colour which is produced when ω-bromobenz-aldehyde-2 : 4-dibromophenylhydrazone alone is warmed with alcoholic potash is probably due to the formation of a similar formazyl compound, the hydrazine in this case being provided by the hydrolysis to benzoic acid and 2 : 4-dibromophenylhydrazine, thus :

$$C_6H_3Br_2 \cdot NH \cdot N{:}CPhBr \xrightarrow{HOH} C_6H_3Br_2 \cdot NH \cdot NH \cdot COPh \xrightarrow{HOH}$$
$$C_6H_3Br_2 \cdot NH \cdot NH_2 + PhCO_2H,$$
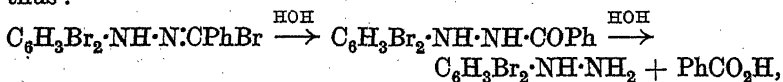
the further reaction of the dibromophenylhydrazine with some of the original substance producing the coloured tetrabromoformazyl compound, $C_6H_3Br_2 \cdot NH \cdot N{:}CPh \cdot N{:}N \cdot C_6H_3Br_2$.

The presence of sodium acetate in the acetic acid solution during the bromination of benzaldehydephenylhydrazone entirely changes the course of the reaction. When 2 mols. of bromine, 1 mol. of the hydrazone, and an excess of sodium acetate are employed, the product is not ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone, but a sparingly soluble, yellow compound, which has a composition and molecular weight represented by the formula $C_{26}H_{18}N_4Br_2$. This has been shown to be 1 : 4-di-*p*-bromophenyl-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine (III), formed from 2 mols. of the hydrazone as indicated below :

$$\begin{array}{cc} C_6H_5 \cdot CH{:}N \cdot NH \cdot C_6H_5 \\ C_6H_5 \cdot NH \cdot N{:}CH \cdot C_6H_5 \end{array} \xrightarrow{4Br_2} \begin{array}{cc} C_6H_5 \cdot \overset{|}{C}{:}N \cdot N \cdot C_6H_4Br \\ C_6H_4Br \cdot N \cdot N{:}\overset{|}{C} \cdot C_6H_5 \end{array} \text{(III.),}$$
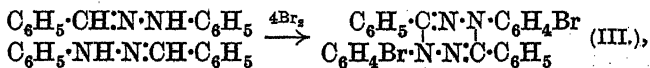
since on dry distillation alone or with zinc dust it yields benzonitrile, whilst energetic reduction gives p-bromoaniline, showing that the bromine is in the p-position in the nucleus attached to the nitrogen atom.

The compound is also formed by the action of bromine under similar conditions upon either benzaldehyde-p-bromophenyl-hydrazone or ω-chlorobenzaldehydephenylhydrazone :

$$C_6H_5 \cdot CH\!:\!N \cdot NH \cdot C_6H_4Br \xrightarrow{2Br_2} (III.) \xleftarrow{2Br_2} C_6H_5 \cdot CCl\!:\!N \cdot NH \cdot C_6H_5$$
$$C_6H_4Br \cdot NH \cdot N\!:\!CH \cdot C_6H_5 \qquad\qquad C_6H_5 \cdot NH \cdot N\!:\!CCl \cdot C_6H_5$$
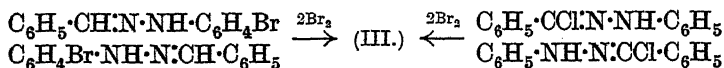
The action of bromine upon benzaldehyde-2 : 4-dibromophenyl-hydrazone in the presence of excess of sodium acetate yields a small amount of the corresponding 2 : 4-dibromo-substituted tetraphenyl-dihydrotetrazine, $\begin{array}{c}C_6H_5 \cdot C\!:\!N \cdot N \cdot C_6H_3Br_2\\ C_6H_3Br_2 \cdot N\!:\!N \cdot C \cdot C_6H_5\end{array}$, together with a larger amount of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone.

This   1 : 4-di(2 : 4-dibromophenyl)-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine resembles in its yellow colour and reactions the 1 : 4-di-p-bromophenyl-3 : 6-diphenyldihydrotetrazine already described.

A mixture of both these derivatives is produced when 3 mols. of bromine are allowed to act upon 1 mol. of benzaldehydephenyl-hydrazone in the presence of an excess of sodium acetate.

Since in the absence of sodium acetate the product of bromination of benzaldehydephenylhydrazone is the ω-bromo-derivative, $C_6H_3Br_2 \cdot NH \cdot N\!:\!CPhBr$, it is probable that in the presence of sodium acetate the formation of the dihydrotetrazine takes place by the elimination of 2HBr from 2 mols. of an ω-bromo-compound in the following manner :

$$2C_6H_5 \cdot NH \cdot N\!:\!CH \cdot C_6H_5 \xrightarrow{4Br_2} \begin{bmatrix} C_6H_4Br \cdot NH \cdot N\!:\!CBr \cdot C_6H_5 \\ C_6H_5 \cdot CBr\!:\!N \cdot NH \cdot C_6H_4Br \end{bmatrix}^{-2HBr} \longrightarrow$$
$$\begin{array}{c} C_6H_4Br \cdot N \cdot N\!:\!C \cdot C_6H_5 \\ C_6H_5 \cdot C\!:\!N \cdot N \cdot C_6H_4Br \end{array}.$$
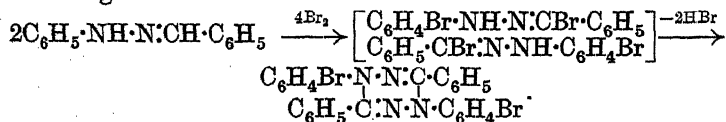
This would account for the comparatively good yield, and single nature of the product.

Bowack and Lapworth (J., 1905, 87, 1857) have shown that ω-halogen compounds derived from oxalic acid can be converted into the dihydrotetrazines with great ease by the action of alkalis; e.g.,

$$\begin{array}{c} C_6H_5 \cdot NH \cdot N\!:\!CBr \cdot CO_2Et \\ EtO_2C \cdot CBr\!:\!N \cdot NH \cdot C_6H_5 \end{array} \longrightarrow \begin{array}{c} C_6H_5 \cdot N \cdot N\!:\!C \cdot CO_2Et \\ EtO_2C \cdot C\!:\!N \cdot N \cdot C_6H_5 \end{array},$$
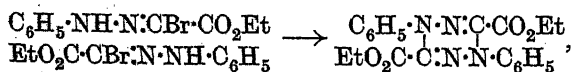
but so far attempts to obtain tetraphenyldihydrotetrazines in a similar way from either ω-bromobenzaldehyde-2 : 4-dibromophenyl-hydrazone or ω-chlorobenzaldehydephenylhydrazone have failed.

We have already shown that the action of acetic acid and sodium acetate alone upon ω-bromobenzaldehyde-2 : 4-dibromo-phenylhydrazone results in the formation of an acetylbenzoyl-phenylhydrazine, no dihydrotetrazine being produced, whereas the action of bromine on ω-chlorobenzaldehydephenylhydrazone in the presence of sodium acetate gives a theoretical yield of the *p*-bromo-substituted tetraphenyldihydrotetrazine (III).

It would seem, therefore, that in the formation of the *p*-bromo-substituted tetraphenyldihydrotetrazine from ω-chlorobenzaldehyde-phenylhydrazone or from benzaldehydephenylhydrazone we cannot regard the substituting action of the bromine and the formation of the heterocyclic ring as two separate and independent processes.

EXPERIMENTAL.

ω-Bromobenzaldehyde-2 : 4-dibromophenylhydrazone (II).—Benz-aldehydephenylhydrazone (20 g.) was suspended in 200 c.c. of glacial acetic acid, and a solution of 49 g. (3 mols.) of bromine in acetic acid gradually added. The hydrazone dissolved, and a thick yellow precipitate separated. This is probably an addition com-pound of bromine with the dibromo-substituted hydrazone, $C_6H_3Br_2 \cdot NH \cdot NBr \cdot CHBrPh$, since on exposure to the atmosphere, or on washing with water, it whitens, losing hydrogen bromide and forming the ω-bromo-compound.

It was separated, washed with water until quite white, and the product recrystallised from acetic acid, separating in long, colourless needles, m. p. 114° (Found : Br, 55·5. Calc., Br, 55·4%).

Preparation of ω-Bromobenzaldehyde-2 : 4-dibromophenylhydrazone from β-Benzoyl-2 : 4-dibromophenylhydrazine by the Action of Phos-phorus Pentabromide.—To 3·5 g. (1 mol.) of β-benzoyl-2 : 4-dibromo-phenylhydrazine dissolved in 15 g. (6 mols.) of phosphorus tri-bromide,* 8 g. (2 mols.) of phosphorus pentabromide were added, and the mixture was warmed gently on a water-bath. The reddish-brown viscid liquid that remained when the evolution of hydrogen bromide had ceased was dissolved in ether, and the solution gradually added to 50 c.c. of methyl alcohol. The ether was evaporated off, and on cooling the resulting alcoholic solution a mass of fine crystals separated. These were recrystallised from acetic acid. They proved to be identical in appearance, properties, and melting point (114°) with the bromination product of benzaldehydephenyl-

* β-Benzoyl-2 : 4-dibromophenylhydrazine does not react with phosphorus tribromide even when boiled with it, at 170°, for some hours. The use of the pentabromide alone is not desirable, since at 100° it is appreciably dis-sociated into the tribromide and free bromine. The presence of an excess of the tribromide almost entirely prevents this.

hydrazone. Yield, 1 g. A little of the substance treated with
ammonia in alcoholic solution yielded benzaldehyde-2 : 4-dibromo-
phenylhydrazidine, m. p. 115° (p. 981).

p-*Bromobenzaldehyde - 2 : 4 - dibromophenylhydrazone.* — p-Bromo-
benzaldehyde (2 g.), prepared from p-bromotoluene by the Etard
method (*Ber.*, 1896, 29, 153), was added to a hot solution of 3 g.
of 2 : 4-dibromophenylhydrazine hydrochloride and 1 g. of sodium
acetate in acetic acid. On cooling, the hydrazone separated as a
pulp of fine crystals. It crystallised from alcohol in fine, white
needles, m. p. 126° (Found : Br, 55·65. $C_{13}H_9N_2Br_3$ requires
Br, 55·4%).

A mixture of this compound with ω-bromobenzaldehyde-2 : 4-
dibromophenylhydrazone (m. p. 114°) melted at 95°.

Reaction of ω-*Bromobenzaldehyde-2 : 4-dibromophenylhydrazone with
Sodium Acetate and Acetic Acid.*—A mixture of 5 g. of ω-bromo-
benzaldehyde-2 : 4-dibromophenylhydrazone and 5 g. of fused and
powdered sodium acetate was boiled with 100 c.c. of acetic acid.
Sodium bromide slowly separated, and after 2 hours the colourless
solution was cooled and poured into water. The white, amorphous
precipitate crystallised * from alcohol in short, colourless, well-
developed prisms, m. p. 158—159°. It is easily soluble in acetic
acid, chloroform, or benzene. An analysis showed that one bromine
of the original compound had been replaced by the group $C_2H_3O_2$
(Found : Br, 38·9%. $C_{15}H_{12}O_2N_2Br_2$ requires Br, 38·8%).

Two g. of the substance were boiled for 2 hours with a mixture
of 20 c.c. of alcohol and 20 c.c. of concentrated hydrochloric acid.
The colourless solution on cooling deposited long, white needles,
which were shown to be the hydrochloride of 2 : 4-dibromophenyl-
hydrazine by conversion into the characteristic bright red *o*-nitro-
benzaldehyde-2 : 4-dibromophenylhydrazone, m. p. 205°.

The mother-liquor from the hydrolysis, which smelt strongly of
ethyl acetate, was made slightly alkaline with caustic soda, and the
alcohol distilled off. The resulting solution was acidified with
hydrochloric acid, and allowed to cool, when colourless crystals
of benzoic acid (m. p. 121°) separated. The hydrolysis of the
compound in this way to 2 : 4-dibromophenylhydrazine, acetic
acid, and benzoic acid indicated that it was probably an acetyl-
benzoyl-2 : 4-dibromophenylhydrazine, $C_6H_3Br_2 \cdot NAc \cdot NH \cdot COPh$.
This constitution was further established by the direct synthesis of
the compound from 2 : 4-dibromophenylhydrazine.

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* The amorphous solid first formed melts indefinitely below 100° and is
extremely soluble in most organic solvents. In recrystallising, it was essential
to seed the solution with crystals previously obtained by allowing a little of
the substance to stand in contact with a few drops of acetic acid for some days.

This hydrazine (5 g.) was benzoylated by the method of Schotten and Baumann. The insoluble product, β-benzoyl-α-2 : 4-dibromophenylhydrazine, $C_6H_3Br_2 \cdot NH \cdot NH \cdot CO \cdot C_6H_5$, crystallised from alcohol in colourless needles, m. p. 172° (Found : Br, 43·25. $C_{13}H_{10}ON_2Br_2$ requires Br, 43·2%). The acetyl derivative, prepared by boiling 1 g. of this compound for a few minutes with equal parts of acetyl chloride and acetic acid, was identical in melting point (158—159°), appearance, and properties with, and did not depress the melting point of, the substance obtained from ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone.

Benzaldehyde - 2 : 4 - dibromophenylhydrazidine. — Concentrated aqueous ammonia (5 c.c.) was added to a suspension of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone (5 g.) in 50 c.c. of alcohol, and the mixture gently warmed until all had dissolved. The light brown solution was poured into water, when the hydrazidine slowly separated as a semi-solid mass, which was recrystallised from alcohol. It separated in colourless, compact, six-sided prisms, m. p. 115°. It is easily soluble in most organic solvents, sparingly soluble in ligroin, and insoluble in water (Found : Br, 43·4. $C_{13}H_{11}N_3Br_2$ requires Br, 43·3%).

The hydrochloride of this hydrazidine, obtained by cooling a hot solution of 5 g. of the base in 50 c.c. of alcohol and an equal volume of concentrated hydrochloric acid, forms glistening, white, rectangular plates, m. p. 260° (decomp.). It is moderately soluble in alcohol and sparingly soluble in water (Found : Cl + Br, 47·9. $C_{13}H_{12}N_3ClBr_2$ requires Cl + Br, 48·2%).

The constitution of this hydrazidine was confirmed by its synthesis from ω-chlorobenzaldehydephenylhydrazone.

The hydrazone (5 g.), prepared from phosphorus pentachloride and β-benzoylphenylhydrazine by Pechmann's method (*Ber.*, 1894, 27, 2122), was suspended in acetic acid and a solution of 8 g. (2 mols.) of bromine in acetic acid slowly added. The yellow precipitate of *ω-chlorobenzaldehyde-2 : 4-dibromophenylhydrazone* crystallised from acetic acid in colourless needles, m. p. 109° (Found : Cl + Br, 50·45. $C_{13}H_9N_2ClBr_2$ requires Cl + Br, 50·2%).

The action of ammonia upon it is precisely similar to its action upon the ω-bromo-compound, benzaldehyde-2 : 4-dibromophenylhydrazidine being formed.

ω-Cyanobenzaldehyde-2 : 4-dibromophenylhydrazone,

$$C_6H_3Br_2 \cdot NH \cdot N \colon CPh \cdot CN.$$
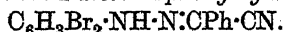
—A solution of 5 g. of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone in 50 c.c. of boiling alcohol was boiled with a solution of 2 g. of potassium cyanide in 5 c.c. of water for ½ hour, and on cooling, faintly yellow crystals of the cyano-compound separated.

They were washed with a little hot water, dried, and recrystallised from boiling alcohol, in which they were moderately soluble.

This compound is polymorphic, and separates from alcoholic solutions first in long, pale yellow, hair-like crystals, which fill the entire liquid. These, if left in the solvent at the ordinary temperature, slowly redissolve, transforming into stouter crystals of a somewhat deeper shade of yellow, which finally sink to a compact layer upon the bottom of the containing vessel. The complete transformation requires about 2 days. Both forms melt at 139° (Found : Br, 42·3. $C_{14}H_9N_3Br_2$ requires Br, 42·2%).

Dibromoformazylbenzene, $C_6H_3Br_2 \cdot NH \cdot N \vdots CPh \cdot N \vdots NPh$.—To 5 g. (1 mol.) of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone suspended in 50 c.c. of alcohol, an excess, 5 g., of phenylhydrazine was added, and the mixture boiled for 15 minutes. The solution quickly developed a deep red coloration, and dark crystals of the formazyl derivative separated. It crystallised from boiling acetic acid in small clusters of reddish-brown needles, m. p. 173—174° (Found : N, 12·4; Br, 35·0. $C_{19}H_{14}N_4Br_2$ requires N, 12·2; Br, 34·9%).

Formation of Substituted Tetraphenyldihydrotetrazines. 1 : 4-*Di-p-bromophenyl*-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine* (III).—Twenty g. (1 mol.) of benzaldehydephenylhydrazone and 40 g. (5 mols.) of fused and finely powdered sodium acetate were made into a thin paste with acetic acid, cooled, and a solution of 32 g. (2 mols.) of bromine in 50 c.c. of acetic acid added in small portions. The yellow solution slowly deposited a mixture of sodium bromide and fine yellow crystals of the dihydrotetrazine. After a few hours, the precipitate was collected, washed with hot water, and recrystallised from acetic acid, separating very slowly in well-formed, bright yellow prisms, m. p. 265° : Yield 13 g., 50% of the theoretical. The tetrazine is almost insoluble in alcohol or ligroin, and only moderately soluble in benzene or chloroform (Found : C, 57·6; H, 3·5; N, 10·3; Br, 29·3; M, cryoscopic in benzene, 535. $C_{13}H_9N_2Br$ requires C, 57·15; H, 3·3; N, 10·3; Br, 29·2%; M, 546).

The substance dissolves in concentrated sulphuric acid, giving a yellow solution, which changes to deep blue when a trace of nitric acid or other oxidising agent is added. When energetically reduced in acetic acid solution by concentrated hydrochloric acid and zinc, a clear solution was obtained which yielded *p*-bromoaniline on making alkaline and steam distilling.

On strongly heating above its melting point, it decomposed and benzonitrile (b. p. 188°, yielding benzoic acid on hydrolysis) distilled over. When an intimate mixture of the compound with

zinc dust (4 parts) was distilled in the same way, benzonitrile distilled over as before, and in addition a quantity of ammonia was evolved.

Preparation of 1 : 4-*Di*-p-*bromophenyl*-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine* (a) *from Benzaldehyde*-p-*bromophenylhydrazone.* —To a solution of 2·7 g. (1 mol.) of benzaldehyde-*p*-bromophenylhydrazone and 6 g. of powdered anhydrous sodium acetate in 100 c.c. of acetic acid, a solution of 1·6 g. (1 mol.) of bromine in acetic acid was gradually added. The solution on standing deposited fine, yellow crystals which when washed free of sodium bromide and recrystallised from acetic acid melted at 265°, and were identical in appearance and properties with 1 : 4-di-*p*-bromophenyl-3 : 6-diphenyl-1 : 4-dihydrotetrazine (m. p. 265°) prepared from benzaldehydephenylhydrazone. Yield 1 g.

(b) *From* ω-*Chlorobenzaldehydephenylhydrazone.*—To a fine suspension of 6 g. (1 mol.) of the hydrazone and 10 g. (5 mols.) of fused and powdered sodium acetate in acetic acid, a solution of 4 g. (1 mol.) of bromine in acetic acid was slowly added, a light brown solution being formed. This, on standing, deposited a mixture of sodium bromide and yellow crystals of the dihydrotetrazine. These were washed first with a little alcohol and then with hot water, and dried. The compound was practically pure, and the yield, 6 g., 90% of the theoretical.

Preparation of 1 : 4-*Di*(2 : 4-*dibromophenyl*)-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine from Benzaldehyde*-2 : 4-*dibromophenylhydrazone.*—A solution of 2 g. (1 mol.) of bromine in acetic acid was added to a suspension of 5 g. (1 mol.) of benzaldehyde-2 : 4-dibromophenylhydrazone and 10 g. of fused and powdered sodium acetate in the same solvent. The hydrazone dissolved, and white crystals of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone separated. No dihydrotetrazine could be isolated, and the sodium acetate did not appear to have affected the normal course of the reaction.

The use of a larger proportion of bromine, however, under similar conditions resulted in the formation of small quantities of the dihydrotetrazine.

Five g. (1 mol.) of benzaldehyde-2 : 4-dibromophenylhydrazone and 10 g. of sodium acetate were made into a fine paste with acetic acid, and 4 g. (2 mols.) of bromine in acetic acid were gradually added. The hydrazone dissolved and towards the end of the addition a thick, yellow precipitate separated. This was washed with water, and extracted with 50 c.c. of boiling alcohol, when the greater part passed into solution, leaving a fine, yellow, insoluble residue. The hot alcoholic solution, on cooling, deposited colourless crystals of ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone,

m. p. 114°. The yellow residue crystallised from acetic acid, in which it was somewhat sparingly soluble, in glistening, irregular, pale yellow leaflets, m. p. 255°. Yield 0·6 g. The use of a larger proportion of bromine did not improve the yield further. The compound is almost insoluble in alcohol or ligroin, and only moderately soluble in benzene or chloroform (Found: N, 7·8; Br, 45·4; M, ebullioscopic in chloroform, 674. $C_{26}H_{16}N_4Br_4$ requires N, 8·0; Br, 45·4%; M, 704).

Like the corresponding p-bromophenyl-compound described above, it dissolves in sulphuric acid, giving a yellow solution which changes to a vivid blue when an oxidising agent is added. It decomposes in a similar manner on dry distillation, yielding benzonitrile, showing that no substitution has taken place in the original benzaldehyde nucleus.

Formation of 1 : 4-*Di*-p-*bromophenyl*- *and* 1 : 4-*Di*(2 : 4-*dibromophenyl*)-3 : 6-*diphenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine by the Action of Bromine* (3 *mols.*) *upon Benzaldehydephenylhydrazone in Presence of Sodium Acetate.*—When to the yellow mixture obtained by adding 32 g. (2 mols.) of bromine to 20 g. (1 mol.) of benzaldehydephenylhydrazone and 40 g. of sodium acetate in acetic acid, a further 16 g. (1 mol.) of bromine dissolved in acetic acid were added, the solution darkened, and a blackish solid was deposited. This was separated, washed with hot water, and dissolved in about a litre of boiling acetic acid. A dark solution was formed and some bromine vapour was evolved. On cooling, a mixture of the two bromo-substituted tetraphenyldihydrotetrazines was deposited as yellow crystals. After four recrystallisations from boiling acetic acid the di-p-bromophenyldiphenyldihydrotetrazine (m. p. 265°) was obtained in a pure condition (yield 3—4 g.). The mother-liquors from the first of these operations were diluted with alcohol, and on standing deposited light yellow leaflets of the di(2 : 4-dibromophenyl)diphenyldihydrotetrazine, together with a few heavier compact prisms of the preceding dihydrotetrazine. A rough separation was effected by mechanically washing off the lighter leaflets with a little alcohol, and these were then purified by four recrystallisations from acetic acid. Yield, nearly 0·5 g. The product thus obtained melted at 255°, and proved to be identical with 1 : 4-di(dibromophenyl)-3 : 6-diphenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine obtained from benzaldehyde-2 : 4-dibromophenylhydrazone.

CXXXIV.—*Ring-chain Tautomerism. Part XIII. Three-carbon Ring-chain Tautomerism in a Bridged Ring System.*

By JOHN WILLIAM BAKER.

IT has been pointed out (Ingold, Perren, and Thorpe, J., 1922, **121**, 1765) that whenever the groups $>C\!:\!C\cdot CO_2Et$ and $[H]\overset{|}{C}\cdot CO_2Et$ required for Michael's addition reaction are present in the same molecule, three-carbon tautomerism may result. The tautomeric change is of the glutaconic type (A) or of the ring-chain three-carbon type (B) according as the groups are contiguous or not.

$$CO_2Et\cdot[H]\overset{|}{C}\text{——}\overset{|}{C}\!:\!\overset{|}{C}\cdot CO_2Et \rightleftharpoons CO_2Et\cdot\overset{|}{C}\text{===}\overset{|}{C}\cdot C[H]\cdot CO_2Et \quad (A)$$

$$CO_2Et\cdot[H]\overset{|}{C}\overset{[CH_2]_n}{\diagdown}\overset{|}{C}\!:\!C\cdot CO_2Et \rightleftharpoons CO_2Et\cdot\overset{|}{C}\overset{[CH_2]_n}{\diagdown}\overset{|}{C}\cdot C[H]\cdot CO_2Et \quad (B)$$
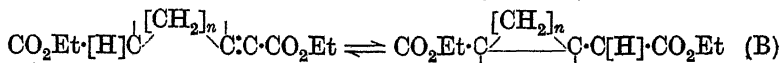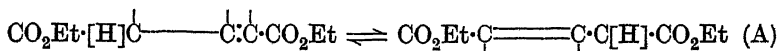
The reaction of type B for which $n = 2$ has already been investigated (*loc. cit.*). The examination of the simpler type ($n = 1$) forms the subject of this paper.

In all experiments of this kind a difficulty arises from the instability of the alicyclic ring when an easy path is provided for its fission. This may be overcome (as has previously been shown) by the introduction of bulky substituents, but in the present case the device was adopted of enclosing two of the valencies of the *cyclo*propane ring in a *cyclo*hexane ring; the stability of the structure (I) thus produced appears to be guaranteed by the occurrence of Δ^3- and Δ^4-carene (II and III) in nature (Simonsen, J., 1920, **117**, 570; 1922, **121**, 2292).

$$>C\overset{\text{C—C—C}}{\underset{\text{C—C—C}}{<}}\qquad Me_2C\overset{\text{CH·CH}_2·\text{CH}}{\underset{\text{CH·CH}_2·\text{CMe}}{<}}\qquad Me_2C\overset{\text{CH·CH}_2·\text{CH}_2}{\underset{\text{CH·CH=CMe}}{<}}$$
$$\text{(I.)}\qquad\qquad\qquad\text{(II.)}\qquad\qquad\qquad\text{(III.)}$$
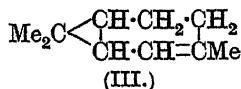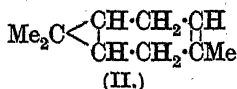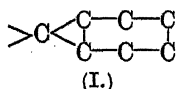
Since carene on treatment with an ethereal solution of hydrogen chloride is converted into sylvestrene hydrochloride, fission of the *cyclo*propane ring occurring, the existence of tautomeric interchange between the *cyclo*hexene derivative (IV) (p. 987) and the *bicyclo*heptane compound (V) seemed highly probable.

A rational synthesis of the unsaturated, open-chain form (IV) of the ester was effected by condensing the dibromo-addition product of ethyl Δ^1-*cyclo*hexeneacetate (VI) with sodiomalonic ester. The first action appears to be the elimination of hydrogen bromide with the formation of the bromo-compound (VII) (which

was isolated), and this, reacting with a molecule of sodiomalonic ester, yields the required Δ^1-*cyclo*hexene-1-acetate-2-malonate (IV).

$$
\begin{array}{ccc}
\text{CH}_2 & & \text{CH}_2 \\
\text{H}_2\text{C} \diagup \quad \diagdown \text{CBr·CH}_2\text{·CO}_2\text{Et} & & \text{H}_2\text{C} \diagup \quad \diagdown \text{C·CH}_2\text{·CO}_2\text{Et} \xrightarrow{\text{CHNa(CO}_2\text{Et)}_2} \text{(IV.)} \\
\text{H}_2\text{C} \diagdown \quad \diagup \text{CHBr} & \longrightarrow & \text{H}_2\text{C} \diagdown \quad \diagup \text{CBr} \\
\text{CH}_2 & & \text{CH}_2 \\
\text{(VI.)} & & \text{(VII.)}
\end{array}
$$
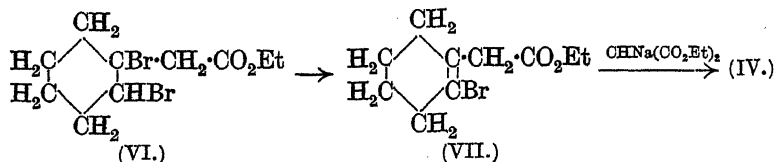
Clear evidence of the existence of ring-chain tautomerism in this ester has been obtained, since, under different conditions, unsaturated products derived from the open-chain form (IV) and saturated products derived from the dicyclic form (V) were isolated in yields which exclude the possibility that the ester is merely a static mixture of the two forms.

Hydrolysis of the parent ester (IV or V) with 4N-alcoholic potash yields the *unsaturated*, tricarboxylic acid (VIII), derived from the open-chain form, the yield, after purification, amounting to 69%, calculated on the assumption that the ester exists entirely in its unsaturated form. On regulated oxidation with an alkaline solution of permanganate in the cold, this acid yields a lactone derivative (IX) of the dihydroxy-acid, which can also be isolated, in small yield as a by-product, from the gum obtained as the product of hydrolysis of the ozonide of the parent ester; and, in the latter case, the absence of any side-chain fission products proves that the double bond is not extracyclic.

On the other hand, hydrolysis of the parent ester (IV) or (V) with 20% hydrochloric acid yields the fully *saturated* dicarboxylic acid (X) corresponding to the dicyclic form of the ester, carbon dioxide having been eliminated during the hydrolysis.

$$
\begin{array}{cc}
& \text{CH}_2 \quad \diagup \text{CH}_2\text{·CO}_2\text{H} \\
\text{(IX.)} \quad \text{H}_2\text{C} \diagup \quad \diagdown \text{C} \!\!-\!\!-\!\!-\!\!-\!\!-\!\!\text{O} \\
\text{H}_2\text{C} \diagdown \quad \diagup \text{C(OH)·CH}_2\text{·CO} \\
\text{CH}_2
\end{array}
$$
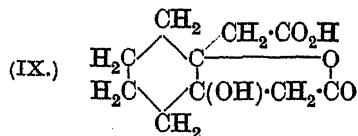
This acid is only slowly attacked even by boiling potassium permanganate in acid solution, and the yield of crystalline material amounts to 34%, calculated on the assumption that the ester existed entirely in its dicyclic form (V). The combined yields of the two acids resulting, respectively, from the hydrolysis of the open-chain and dicyclic forms of the ester amount to more than 100%, thus excluding any possibility that the parent ester is a static mixture of the two forms.

On treatment with 20% hydrochloric acid the *unsaturated*,

tricarboxylic acid (VIII) is converted into the *saturated*, dicarboxylic acid (X), this reagent being capable of effecting the irreversible change between the two solid acids which is analogous to the reversible change producing tautomeric equilibrium in the liquid ester.

On fusion, the tricarboxylic acid (VIII) loses a molecule of carbon dioxide and is converted, not into the saturated acid (X), but, mainly at least (see footnote, p. 990) into an isomeric, unsaturated acid (XI).

These results, which are summarised below, can be explained only by the existence, in the parent ester, of a tautomeric equilibrium such as was previously postulated between open-chain and dicyclic forms.

$$
\text{(V.)} \quad
\begin{array}{l}
CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CO_2Et \\
| \qquad \qquad | {>} C(CO_2Et)_2 \\
CH_2 \cdot CH_2 \cdot CH
\end{array}
\quad \rightleftharpoons \quad
\begin{array}{l}
CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CO_2Et \\
| \qquad \qquad || \\
CH_2 \cdot CH_2 \cdot C \cdot CH(CO_2Et)_2
\end{array}
\quad \text{(IV.)}
$$

b. p. 210/10 mm.

20% HCl ↓   alc. KOH ↓

$$
\text{(X.)} \quad
\begin{array}{l}
CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CO_2H \\
| \qquad \qquad | {>} CH \cdot CO_2H \\
CH_2 \cdot CH_2 \cdot CH
\end{array}
\quad \xleftarrow{\text{20% HCl}} \quad
\begin{array}{l}
CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CO_2H \\
| \qquad \qquad || \\
CH_2 \cdot CH_2 \cdot C \cdot CH(CO_2H)_2
\end{array}
\quad \text{(VIII.)}
$$

m. p. 186°.   m. p. 210°.

heat ↙

$$
\begin{array}{l}
CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CO_2H \\
| \qquad \qquad || \qquad \quad \text{(XI.)} \\
CH_2 \cdot CH_2 \cdot C \cdot CH_2 \cdot CO_2H
\end{array}
$$

m. p. 122°.
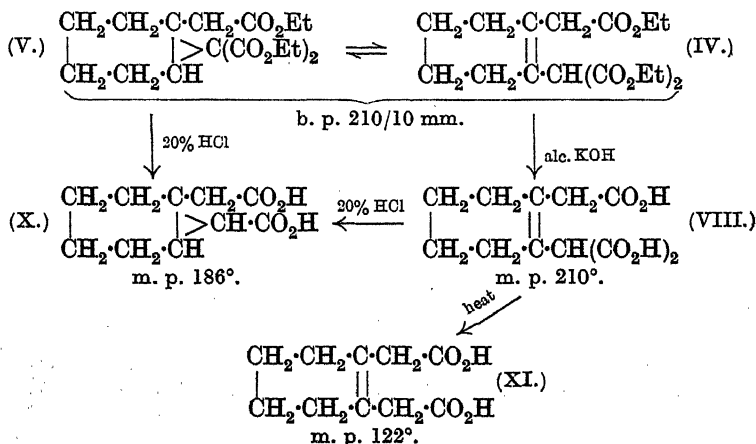
In such a case it would seem possible to estimate the quantity of unsaturated form present by titrating the ester with a standard solution of bromine; this, by removing the unsaturated individual, would disturb the equilibrium, and an initial rapid absorption should be followed by a slower absorption as the equilibrium is re-established with the formation of a further quantity of the unsaturated form. Since, however, no such clear line of demarcation between rapid and slower absorption of bromine could be observed (bromine being fairly rapidly absorbed until the theoretical quantity for 100% of the unsaturated form of the ester had been added), it must be concluded, either that the re-establishment of the equilibrium is too rapid for detection by this method, or that the equilibrium is largely displaced in favour of the unsaturated form. In the latter case the formation of the saturated acid to the extent of 34% can be accomplished only by the con-

version of a large quantity of the unsaturated ester into its saturated,
dicyclic form, and thus, in the opinion of the author, the existence
of ring-chain tautomerism of the three-carbon type has been experi-
mentally established in what is essentially the simplest possible
case, using the *cyclo*hexane ring as the stabilising influence on the
attached *cyclo*propane ring.

EXPERIMENTAL.

Ethyl Δ^1-*cyclo*hexeneacetate was prepared by condensing *cyclo*-
hexanone with bromoacetic ester and zinc in benzene solution
(Reformatsky's method), and dehydrating the hydroxy-ester by
heating with powdered, fused potassium hydrogen sulphate. The
product was fractionated and the fraction, b. p. 118—125°/20 mm.,
used in this investigation.

Ethyl 1 : 2-*Dibromocyclohexane-1-acetate* (VI).—A solution of 20 g.
of bromine in 120 c.c. of chloroform was added slowly to 20 g. of
ethyl Δ^1-*cyclo*hexeneacetate cooled in ice. The solvent was evapor-
ated in a vacuum at the ordinary temperature, and the last traces
were removed in a vacuum desiccator over potash. The crude
substance cannot be distilled (Found : Br, 49·5. $C_{10}H_{16}O_2Br_2$
requires Br, 48·9%).

Condensation of Ethyl 1 : 2-*Dibromocyclohexane-1-acetate with
Ethyl Malonate. Ethyl* 2-*Bromo-*Δ^1-*cyclohexeneacetate* (VII).—The
dibromo-ester (49 g.) was added to a well-cooled mixture of 24 g.
of ethyl malonate and 6·9 g. of sodium dissolved in 150 c.c. of
absolute alcohol, and the whole was heated under reflux for 3
hours. The product, separated from a small quantity of acid
fraction in the usual manner, was purified by fractionation in a
high vacuum, and the fraction, b. p. 128—135°/8 mm., was col-
lected (Found : C, 48·9; H, 6·6; Br, 31·4. $C_{10}H_{15}O_2Br$ requires
C, 48·6; H, 6·1; Br, 32·4%).

Ethyl Δ^1-*cycloHexene-1-acetate-2-malonate* (IV). — The bromo-
compound (VII) (30 g.) was condensed with 30 g. of ethyl
malonate and 4 g. of sodium dissolved in 100 c.c. of absolute alcohol.
The product, worked up as before, was a rather viscous, almost
colourless oil, b. p. 210°/10 mm. (Found : C, 60·9; H, 7·95.
$C_{18}H_{28}O_6$ requires C, 60·9; H, 8·0%).

(a) *Hydrolysis with alcoholic potash.* The ester (IV) (15 g.) was
heated under reflux with a solution of 12 g. of potassium hydroxide
in 75 c.c. of 95% alcohol for several hours. After extraction of
the organic acid in the usual manner, Δ^1-*cyclohexene-1-acetic-2-
malonic acid* (VIII) was obtained from the ethereal solution as a
slightly viscous solid (11·5 g.), from which gummy impurities were
removed by repeated extraction with hot benzene. The white,

solid residue melted at 210° after repeated crystallisation from acetone–chloroform (Found: C, 54·4; H, 5·8; M, by titration, 242·7. $C_{11}H_{14}O_6$ requires C, 54·55; H, 5·8%; M, 241·8).

(b) *Hydrolysis with 20% hydrochloric acid.* The ester (IV) (2·8 g.) was heated under reflux with 40 c.c. of 20% hydrochloric acid for 20 hours. On cooling, the main portion of the acid product (0·5 g.) crystallised. The mother-liquor, on extraction with ether, yielded a gum which slowly deposited a further 0·1 g. of the acid. On recrystallisation from acetone–chloroform, 2-*carboxy*bicyclo-[4,1,0]*heptane-1-acetic acid* (X) was obtained as small rosettes, m. p. 186°. It does not decolorise an alkaline solution of potassium permanganate, or a solution of bromine in chloroform (Found: C, 60·4; H, 7·0. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%). On titration it behaved as a monobasic acid; M, 196·5 (M, calculated for a dibasic acid, 99·0).

Conversion of the Open-chain Unsaturated Acid into the Dicyclic Saturated Acid.—The unsaturated acid (VIII) (0·2 g.) was heated under reflux with 15 c.c. of 20% hydrochloric acid for 24 hours. On cooling, a small quantity of slightly brown, crystalline material separated, which, when purified on porous porcelain, had m. p. 182°, and was proved by its properties and by means of a mixed melting-point determination with a genuine specimen to be the saturated, dicyclic acid (X).

Oxidation of Δ^1-*cycloHexene-1-acetic-2-malonic Acid. Lactone of* 1 : 2-*Dihydroxy*cyclohexane-1 : 2-*diacetic Acid* (IX).—A solution of 1 g. of the acid in 30 c.c. of sodium bicarbonate solution was cooled in ice, and 145 c.c. of $N/8$-potassium permanganate added slowly with constant shaking. After several extractions of the precipitated hydrated manganese dioxide with boiling water, the combined filtrates were concentrated and extracted with ether. The residue from the dried ethereal solution solidified to an almost gum-free mass which, after several crystallisations from ethyl acetate–petroleum (b. p. 60—80°), was obtained in minute needles, m. p. 187° (Found: C, 54·8; H, 6·5. $C_{10}H_{14}O_5$ requires C, 56·0; H, 6·6%). Since there was a possibility of carbon dioxide splitting off incompletely during the experiment, the product was probably contaminated with the lactone of 1 : 2-dihydroxy*cyclo*hexane-1-acetic-2-malonic acid (which requires C, 51·2; H, 5·4%), but with the quantity of material available, complete separation of these two acids by fractional crystallisation was impossible. The presence of a small quantity of the latter would explain the low percentage of carbon obtained in the analysis.

Oxidation of Ethyl Δ^1-*cycloHexene-1-acetate-2-malonate by Ozone.*— When the ozonide obtained from the parent ester was hydrolysed,

no fission products could be detected, the same lactone being the sole product identified.

Δ^1-cyclo*Hexene*-1 : 2-*diacetic Acid* (XI).—This acid is obtained as the chief product * when the acid (VIII) is heated at 215° for 15 minutes. The clear brown gum obtained from about 1 g. dissolved readily, with effervescence, in sodium carbonate solution. The acid, extracted by ether, on recrystallisation from dry benzene, was obtained in small prisms, m. p. 122° (Found : C, 59·9; H, 7·2; M, by titration, 192. $C_{10}H_{14}O_4$ requires C, 60·4; H, 7·0%; M, 198).

Titration of the Parent Ester with Bromine.—An $N/5$-solution of pure bromine in chloroform was added from a burette to 0·937 g. of the ester. The rate of absorption, which was very rapid at first, gradually decreased. When 30 c.c. of the bromine solution had been added, the colour persisted for a long period, hydrogen bromide being slowly given off. The unsaturated form of the ester would require 29·63 c.c. for 0·937 g.

The author wishes to express his gratitude to Prof. C. K. Ingold for suggesting this research and for his valuable advice during its progress.

CXXXV.—*Synthesis of* 5 : 5′-*Dibromo*-6 : 6′-*dimethoxy*-2 : 2′-*bisoxythionaphthen.*

By ROLAND HALL GRIFFITH and EDWARD HOPE.

IN connexion with investigations carried out at various times by one of us on the relation between colour and orientation of substituents in certain types of thioindigoid dyes, the need for more accurate information than any then available became evident.

It is well known that 6 : 6′-diethoxy-2 : 2′-bisoxythionaphthen (I) (" 6 : 6′-Diethoxythioindigo," Helindone Orange R) passes on dibromination into " Helindone Fast Scarlet R "; it is extremely probable that the position of entry of the bromine atoms is either 5 : 5′ or 7 : 7′, but in view of the interesting and marked changes in colour which are known to occur among " thioindigo " derivatives it was desirable to obtain definite evidence. It was further

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* In one or two experiments very small quantities of two other acids, both unsaturated, with m. p.'s 147° and approximately 180°, respectively, were obtained, but not in sufficient quantities for investigation.

worth while to attempt to discover whether, in the event of substitution occurring in one of the likely positions 5 and 7, any difference of colour would be noticeable if 5 were preferred to 7.

(I.) EtO⟨⟩—CO—C=C—CO—⟨⟩OEt
     S   S

[MeO⟨Br⟩—CO—C=⟨⟩]₂ (II.)
        S
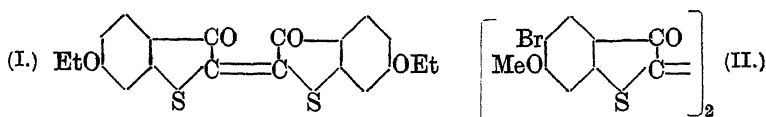
The present communication deals with the synthesis of the compound (II) and describes a number of new derivatives of *p*-tolyl methyl ether. The starting point was *p*-tolyl carbonate, which was nitrated so as to yield, after hydrolysis of the product, 2-nitro-*p*-cresol. This was converted by well-known processes into 5-bromo-2-acetylamino-*p*-tolyl methyl ether (III). After oxidation of the latter to 5-bromo-2-acetylamino-4-methoxybenzoic acid, this substance was converted by the well-known process (D.R.-P. 205450) into 4-bromo-2-carboxy-5-methoxyphenylthiolacetic acid (IV) and thence into the corresponding " thioindigo."

(III.) Me⟨NHAc⟩OMe
            Br

CO₂H⟨S·CH₂·CO₂H⟩OMe (IV.)
        Br
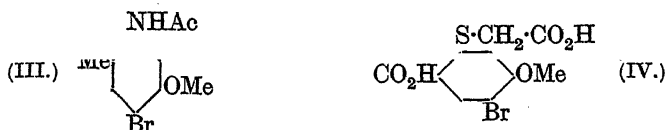
The constitution of the substance (III) was definitely established by elimination of the acetylamino-group and oxidation of the resulting bromomethylanisole to 3-bromoanisic acid; the 2-bromo-acid was also prepared for comparison.

The bromoacetylaminomethoxybenzoic acid obtained by the oxidation of (III) loses carbon dioxide with great ease on boiling with hydrochloric acid; the anthranilic acid has to be prepared by means of alkali. This loss of carbon dioxide is of interest in connexion with the statement of Friedländer (*Annalen*, 1912, **388**, 48) that 4-methoxyanthranilic acid is stable in boiling hydrochloric acid, whereas 6-bromoanthranilic acid loses carbon dioxide like the one here described.

5 : 5′-Dibromo-6 : 6′-dimethoxy-2 : 2′-bisoxythionaphthen (II) is a dye of pure scarlet colour indistinguishable from Helindone Scarlet R. Their absorption spectra are so similar as to suggest an identical constitution. It may be that the replacement of the methoxy-group in (II) by an ethoxy-group will produce a dye with an absorption band identical with that of Helindone Scarlet.

In addition to the " thioindigo," two other dyes have been obtained from the acid (IV); condensation with isatin yields the

substance (V) and a similar reaction with acenaphthenequinone gives the "indigo" (VI).
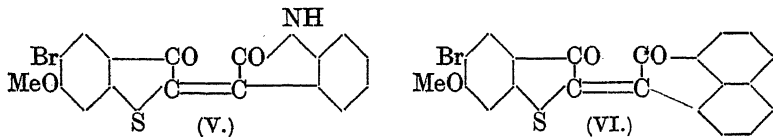
 EXPERIMENTAL.

2-*Acetylamino*-p-*tolyl Methyl Ether*.—The reduction of 2-nitro-p-tolyl methyl ether, which was effected by Limpach with tin and hydrochloric acid (*Ber.*, 1891, **24**, 4140), is more conveniently done with iron and acetic acid. A mixture of 15 g. of the nitro-ether, 4 c.c. of glacial acetic acid, and 250 c.c. of water is stirred to give an emulsion, and iron filings are added at about 70°, at such a rate that the temperature remains at 80—90°. When the reaction is complete the mixture is cooled and extracted with benzene. The crude amine is distilled under reduced pressure; b. p. 140°/20 mm., m. p. 47°.

Acetic anhydride (1·1 equivs.) is added to a solution of the amine in benzene–light petroleum (b. p. 80°), and the mixture heated on a water-bath until reaction begins. The 2-acetylamino-p-tolyl methyl ether remaining after removal of the solvent is distilled under reduced pressure; b. p. 109°/15 mm., m. p. 96° (compare Friedländer, *loc. cit.*).

Bromination.—The acetyl compound (9 g.) is dissolved in 90 g. of acetic acid cooled in ice water, and 8 g. of bromine are run in slowly. After $\frac{1}{2}$ hour, the mixture is poured into water. The 5-bromo-2-acetylamino-p-tolyl methyl ether which separates crystallises from alcohol in white needles, m. p. 191° (Found: Br, 30·5. $C_{10}H_{12}O_2NBr$ requires Br, 31·0%).

Hydrolysis of the Bromo-acetyl Compound (III).—The acetyl compound is boiled with strong hydrochloric acid, ammonia added to the clear solution, and the precipitated amine crystallised from alcohol; m. p. 100° (Found: N, 6·45. $C_8H_{10}ONBr$ requires N, 6·5%). By diazotising and coupling with β-naphthol a scarlet azo-dye is obtained which crystallises from benzene in dark red needles having a green lustre; m. p. 210° (Found: N, 7·5. $C_{18}H_{15}O_2N_2Br$ requires N, 7·55%). The benzoyl derivative of the amine made by the Schotten-Baumann reaction melts at 159°.

Conversion of the Amine into 5-Bromoanisic Acid.—Ten g. of the amine with 100 c.c. of concentrated hydrochloric acid are stirred in a freezing mixture while a solution of 3·5 g. of sodium nitrite

is run in; to the resulting solution 20 g. of stannous chloride dissolved in a minimum of hydrochloric acid are added slowly. After ½ hour, the hydrazine hydrochloride which has separated is washed with hydrochloric acid and treated in hot aqueous solution with excess of sodium acetate. The hydrazine forms pale brown needles, m. p. 192°, from alcohol, which darken on exposure to the air.

The hydrazine (10 g. in dilute acetic acid) is run into a boiling solution of copper sulphate (50 g. in 150 c.c.). Ether extracts from the cold reaction product an oil, b. p. 115°/13 mm., which is probably 3-bromo-*p*-tolyl methyl ether (Schall and Dralle, *Ber.*, 1884, **17**, 2531).

Prolonged boiling of the oil with alkaline permanganate solution gives the salt of an acid; the free acid has a melting point, 217—218°, in agreement with that recorded by Schall and Dralle (*loc. cit.*) for 3-bromoanisic acid; but the 2-bromo-acid is recorded by Balbiano, who does not definitely prove its constitution, as melting at 212°. On account of this uncertainty, this acid has been prepared.

2-Bromoanisic Acid.—2-Bromo-*p*-cresol is easily methylated with methyl sulphate and alkali. The resulting oil is extracted with ether and distilled under reduced pressure; b. p. 114°/16 mm. and 222°/760 mm. It is colourless when pure (Found : Br, 40·5. C_8H_9OBr requires Br, 40·0%).

A suspension of the methyl ether is oxidised with alkaline permanganate, manganese removed by adding alcohol, and the hot liquid filtered and acidified. The white solid obtained is crystallised from alcohol and melts at 199° (Found : Br, 34·8. $C_8H_7O_3Br$ requires Br, 34·6%). Mixed with the acid, m. p. 217°, its melting point is 175—185°; this proves satisfactorily the constitution of the former acid.

5-Bromo-2-acetylamino-4-methoxybenzoic Acid.—The bromo-acetyl compound (III) (13 g.) is ground into a fine paste with water, the whole made up to ½ litre, and the correct amount of magnesium sulphate added. Powdered permanganate is added during about 3 hours to the well-stirred mixture at 85°. The liquid is filtered hot, and addition of acid to the cold filtrate throws down a bulky white precipitate. The acid is recrystallised from alcohol and melts at 253° (yield about 70%) (Found : Br, 27·9. $C_{10}H_{10}O_4NBr$ requires Br, 27·8%).

Hydrolysis with Acid.—By boiling the acetylamino-acid with concentrated hydrochloric acid for about ½ hour a clear solution is obtained, which yields a brown solid on the addition of ammonia. This substance crystallises from boiling water in shining plates,

m. p. 90·5°; it shows no acid character, but is soluble in acids and analysis shows that it is a bromo-anisidine (Found : C, 42·0 ; H, 3·9. C_7H_8ONBr requires C, 41·6; H, 4·0%). In accordance with its method of formation this substance must be 4-*bromo*-m-*anisidine ;* its *benzoyl* derivative melts at 124°.

Hydrolysis with Alkali.—Ten g. of the acetylamino-acid, 5 g. of caustic soda, and 300 c.c. of water are boiled together until a test portion gives a precipitate on the addition of acid which is completely soluble in excess of acid (2—3 hours). The hydrolysis mixture is then cooled and acetic acid added in slight excess. The crude 5-*bromo*-2-*amino*-4-*methoxybenzoic acid* is pale brown and crystallises well from alcohol; m. p. 201°, decomp. 213° (Found : N, 5·7. $C_8H_8O_3NBr$ requires N, 5·7%). The *sodium* salt crystallises in long needles from boiling water (Found : Br, 29·8. $C_8H_7O_3NBrNa$ requires Br, 30·1%). The green *copper* salt is precipitated on adding copper acetate to a faintly acid solution of the anthranilic acid.

5-*Bromo*-4-*methoxy*-2-*thiolbenzoic Acid.*—The amino-acid described above is diazotised by grinding 7·4 g. to a fine paste with 8·7 g. of 30% hydrochloric acid, diluting to 80 c.c., and treating slowly with a solution of 2·1 g. of sodium nitrite, keeping the temperature below 8°. The clear solution is run into a solution of sodium disulphide made from 7·8 g. of $Na_2S,9H_2O$, 1 g. of sulphur, 1·7 g. of caustic soda, and 15 c.c. of water. The mixture is warmed on the water-bath for 1 hour, cooled, and acidified, when di-(bromo-methoxythiosalicylic) acid and sulphur are precipitated. The acid is extracted with aqueous sodium carbonate (2 g.) and precipitated by acid.

The acid is boiled in sodium carbonate solution with zinc dust (4 g.) for 3—4 hours, the mixture treated with 1·4 g. of caustic soda, boiled for a short time, filtered, and acidified. On account of the ease with which 5-bromo-4-methoxy-2-thiolbenzoic acid is oxidised it is better to use the solution of its sodium salt directly for the condensation with chloroacetic acid.

4-*Bromo*-2-*carboxy*-5-*methoxyphenylthiolacetic Acid* (IV).—A solution of the sodium salt from 6·6 g. of the thio-acid is heated, with 100 c.c. of water containing 2·5 g. of chloroacetic acid and sufficient caustic soda to form the sodium salt, on a water-bath for 3 hours. The cold reaction product is acidified and the phenylthiolacetic acid, which separates as a pale brown solid, is crystallised from acetic acid; m. p. 243° (decomp.) (Found : C, 37·15; H, 3·1. $C_{10}H_9O_5BrS$ requires C, 37·4; H, 2·8%).

5 : 5′ - *Dibromo*-6 : 6″ - *dimethoxy* - 2 : 2′ - *bisoxythionaphthen* (II).— The finely powdered thiolacetic acid mixed with fused sodium acetate

(1 part) is warmed with acetic anhydride (10 parts) until reaction begins, after which it will continue for a few minutes with great vigour, leaving a clear solution. The excess of acetic anhydride and the acetic acid are removed under reduced pressure and the solid residue is boiled for 10 minutes with excess of 3% alkali. The resulting solution is filtered, cooled, and treated with potassium ferricyanide solution until no more dye is precipitated. The " thioindigo " is dried on the water-bath and crystallised from nitrobenzene, separating in dark red plates, m. p. 355—360° (Found : C, 42·5; H, 2·2. $C_{18}H_{10}O_4S_2Br_2$ requires C, 42·1; H, 2·0%). From its deep blue solution in concentrated sulphuric acid the dye is reprecipitated on dilution with water in a gelatinous state very suitable for preparation of the vat, which is pale yellow and dyes cloth a good scarlet. The solution in nitrobenzene shows an absorption band with a maximum at $\lambda = 529$. " Helindone Fast Scarlet R " shows a similar band with a maximum at $\lambda = 520$.

Condensation of the Thiolacetic Acid with Isatin and with Acenaphthenequinone.—The acid and isatin are boiled together in equimolecular amount with a large excess of acetic anhydride for 3 hours. The mixture gradually turns dark red and, on cooling, the dye (V) separates in small crystals which are washed with alcohol and crystallised from nitrobenzene; m. p. 315° (Found : C, 52·4; H, 2·85. $C_{17}H_{10}O_3NBrS$ requires C, 52·6; H, 2·6%). The dye has a much bluer shade than the " thioindigo " and its solution in sulphuric acid is purple, but its dyeing properties are unsatisfactory, probably on account of further reaction during reduction.

When the thiolacetic acid is boiled in acetic anhydride solution with acenaphthenequinone, an orange powder separates, which is washed with boiling alcohol; m. p. 337°. Its solution in sulphuric acid is dark brown, and it dyes cloth a good orange from a bright blue vat.

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CXXXVI.—*Some Aromatic Chlorovinylarsines.*

By Arthur Frederick Hunt and Eustace Ebenezer Turner.

Acetylene is slowly absorbed by a solution of anhydrous aluminium chloride in phenyldichloroarsine, to give, after treatment with ice and hydrochloric acid, *phenyl-β-chlorovinylchloroarsine,*

$$AsPhCl \cdot CH{:}CHCl,$$

phenyl-ββ'-dichlorodivinylarsine, $AsPh(CH{:}CHCl)_2$, and compounds of higher boiling point. The last, which have not been investigated further, arise mainly from the intermolecular condensation of phenyldichloroarsine, a process which is preceded by the formation of a crystalline *additive* compound, $AsPhCl_2,AlCl_3$.

If the phenyldichloroarsine–aluminium chloride solution is not cooled during the absorption of acetylene, or if the ice–acid treatment is omitted, β-chlorovinyldichloroarsine and benzene are also formed, in accordance with equations of which the simplest is :

$$AsPhCl \cdot CH{:}CHCl + HCl = PhH + AsCl_2 \cdot CH{:}CHCl.$$

Phenyl-ββ'-dichlorodivinylarsine has also been prepared by the action of magnesium phenyl bromide on ββ'-dichlorodivinylchloroarsine.

The reaction between arsenious chloride and phenylacetylene in presence of aluminium chloride is complicated by the polymerisation of the hydrocarbon, and the only isolable product is a yellow, amorphous substance containing two chlorine atoms to each atom of arsenic. Arsenious chloride, however, combines with phenylacetylene in absence of a catalyst, and from the heavy green oil so obtained, *α-chlorostyryldichloroarsine,* $CPhCl{:}CH \cdot AsCl_2$, and *αα'-dichlorodistyrylchloroarsine,* $(CPhCl{:}CH)_2AsCl$, have been isolated.

Experimental.

Addition of Phenyldichloroarsine to Acetylene.—Acetylene was allowed to bubble through a well-shaken and cooled solution, prepared in the cold, of anhydrous aluminium chloride in phenyl-dichloroarsine. Heat was evolved during the absorption and the latter was found to depend to a considerable extent on the proportion of aluminium chloride used. The results of three experiments are given below :

	I.	II.	III.
Phenyldichloroarsine (grams)	61	58	56
Aluminium chloride (grams)	26	17·5	28·5
Acetylene absorbed (grams)	6	4·5	5·2
Time of absorption (hours)	4·5	4	3

The viscous, greenish-brown product was treated with crushed ice, shaken twice with concentrated hydrochloric acid, separated,

dried over anhydrous sodium sulphate, and separated by distillation into two fractions, b. p. 125—220°/15 mm. and 220—270°/15 mm., respectively. The higher fraction could not be separated into its components, and contained about 8% of chlorine attached to arsenic.

The lower fraction was carefully re-fractionated under diminished pressure with a column, when two fractions, *a* and *b*, were finally collected, in addition to a considerable amount of unchanged phenyldichloroarsine.

Fraction a was practically pure *phenyl-β-chlorovinylchloroarsine*, a pale yellow, unpleasant-smelling liquid, b. p. 140—145°/10 mm. (Found: Cl, attached to arsenic, 14·5. $C_8H_7Cl_2As$ requires Cl, 14·3%). This substance, stable when pure, slowly acquires a violet colour if not carefully freed from the last traces of phenyldichloroarsine.

From *Fraction b*, b. p. 150—170°/10 mm., a pure substance could not be obtained by repeated fractionation alone, but when shaken with aqueous silver nitrate, it gave an *additive* compound, $AsPh(CH:CHCl)_2,AgNO_3$, white needles, m. p. 142° (decomp.) (Found: Ag, 25·0. Calc., Ag, 24·3%). This was crystallised from water, washed with ether, and decomposed with concentrated hydrochloric acid. The resulting almost colourless oil, after being dried and distilled, was pure *phenyl-ββ'-dichlorodivinylarsine*, b. p. 155—160°/10 mm. [Found: Cl (total), 26·0%; *v. infra*].

This substance, which has a nauseating, fishy odour, was also prepared from ββ'-dichlorodivinylchloroarsine (Green and Price, J., 1921, **119**, 448) (15 g.), which reacted vigorously with magnesium phenyl bromide (20% in excess of that theoretically required) in ethereal solution. The whole was kept gently boiling for ½ hour, and then decomposed and worked up in the usual manner, 14·5 g. of phenyl-ββ'-dichlorodivinylarsine being obtained, b. p. 155—160°/10 mm. [Found: Cl (total), 26·2; As, 27·8. $C_{10}H_9Cl_2As$ requires Cl, 25·6; As, 28·0%]. The silver nitrate additive compound was identical with that described above. Phenyl-ββ'-dichlorodivinylarsine forms crystalline *additive* compounds with chloroplatinic acid and with mercuric chloride, and slowly combines with methyl iodide under pressure at 100° to give a gummy methiodide. In an attempt to prepare 1-phenylarsenopyrrole, the arsine was heated in boiling toluene with metallic sodium. Considerable formation of sodium chloride took place, but the product, which contained 19% of chlorine, was not obtained in quantities sufficient for purification.

During the preliminary work on the addition of phenyldichloroarsine to acetylene, the absorption vessel was in some cases allowed

to become warm.   In other experiments, the product was distilled
without previous removal of aluminium chloride.   In both cases,
benzene and β-chlorovinyldichloroarsine (Found : As, 36·5; Cl,
51·3.   Calc., As, 36·1; Cl, 51·3%) were isolated, whilst the higher-
boiling fractions (above 220°/15 mm.), on standing for some weeks,
then decomposed when distilled under diminished pressure, benzene,
arsenious chloride, metallic arsenic, and other products being
formed.

Action of Aluminium Chloride on Phenyldichloroarsine.—A solu-
tion of anhydrous aluminium chloride in cold phenyldichloroarsine
(10 parts), on standing for a few hours, deposited the *additive*
compound, $AsPhCl_2,AlCl_3$, as pale yellow crystals (Found : Al,
38·3.   Calc., Al, 37·5%).   If the additive compound, or a freshly-
prepared solution of aluminium chloride in the chloroarsine is
treated with hydrochloric acid, etc., phenyldichloroarsine is re-
covered unchanged, but if the solution is kept for more than a
few hours, a mixture of products results, the boiling point, ranging
from 130° to 270° at 15 mm., being higher the longer the solution
stands.

Addition of Arsenious Chloride to Phenylacetylene.—The yellow
liquid obtained by mixing phenylacetylene (10 g.), arsenious chloride
(40 g.), and anhydrous aluminium chloride (13 g.), when left at the
ordinary temperature, became green, then violet, and, after 2 hours,
black and viscous.   Extraction of the product after the usual acid
treatment, followed by precipitation with alcohol, gave a yellow,
amorphous solid of indefinite m. p. [Found : As, 5·2; Cl, 4·9%;
whence As : Cl (atoms) = 1 : 2].   A similar product was obtained
when the addition was carried out at − 20°, or when an excess
of arsenious chloride was used.

When phenylacetylene (37 g.) and arsenious chloride (105 g.)
were mixed, some heat was evolved; the mixture, after being
heated at 110° for 4 hours, became a heavy green oil.   The same
result was obtained when the original mixture was left at the
ordinary temperature for a few weeks.   The green oil was shaken
with concentrated hydrochloric acid, etc., and distilled under
diminished pressure, when two small, but definite, fractions were
obtained.   These, on redistillation, gave, respectively, (*a*) *α-chloro-
styryldichloroarsine*, a fairly mobile, slightly fuming, yellowish-
green oil, b. p. 108—110°/12 mm. [Found : Cl (attached to arsenic),
24·4. $C_8H_6Cl_3As$ requires Cl, 25·0%], and (*b*) *αα′-dichlorodistyryl-
chloroarsine*, an olive-green, viscous liquid, b. p. 170—175°/12 mm.
[Found : Cl (attached to arsenic), 9·8. $C_{16}H_{12}Cl_3As$ requires Cl,
9·2%].   Neither arsine possessed an unpleasant odour nor vesicant
properties.

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CXXXVII.—*Tesla-luminescence Spectra. Part V. Some Polynuclear Hydrocarbons.*

By WILLIAM HAMILTON MCVICKER, JOSEPH KENNETH MARSH, and ALFRED WALTER STEWART.

IN previous papers (J., 1923, **123**, 642, 817, 2147; 1924, **125**, 1743) accounts were given of the spectra emitted under the Tesla discharge by the vapours of benzene and a number of its substitution products. In the present communication the work is extended into the field of polynuclear benzene derivatives and so falls into two parts : first, the spectra of compounds containing two or more isolated benzene rings; and, secondly, the spectra of compounds containing fused rings, such as anthracene and acenaphthene.

The apparatus used is the same as before. The figures given below are wave-lengths. The estimates for the lengths of the various spectra are approximate : the spectra often fade off gradually, and at the red end of the spectrum especially (owing to the small dispersion) it is difficult to determine exactly where the band of light terminates. Other factors involved are the different sensitivity of the photographic plate in various regions and the length of the exposure given. In the results below, the exposure was 15 minutes except where some other period is specially mentioned.

I. *Compounds with Two or More Isolated Benzene Rings.*

1. *Diphenyl*, b. p. 253·8—254·4°/759 mm. A faint continuous spectrum extending from about 2890 to 3900 Å.U., fading off gradually at both ends, with indications of very diffuse bands at 3025 and 3130 Å.U.

2. *Diphenylmethane*, b. p. 261·0—261·8°/745 mm. A medium continuous spectrum running from a fairly distinct head at 2673, to 3900 Å.U. The ultra-violet end of the spectrum is abrupt, whilst the other end fades off gradually. There are indications of very indistinct diffuse heads of bands at about 2736 and 2812 Å.U.

3. *Triphenylmethane.* This substance was obtained pure by a series of recrystallisations from alcohol to remove the by-products of the Friedel–Crafts reaction.

M M*

A medium continuous spectrum extending from about 2730 to 4390 Å.U., fading off gradually at both ends, with indications of very diffuse, indistinct heads of bands at about 2820 and 3010 Å.U.

4. *Dibenzyl*, m. p. 53·4°. A faint continuous spectrum running from 2700 to 4300 Å.U. with a brighter region from about 3390 (which is a diffuse head) to 3950 Å.U.

5. *Stilbene*, b. p. 305·0—307·5°/744 mm. A medium continuous spectrum running from about 3100 to 4680 Å.U., and fading off more gradually at the end of greater wave-length. There are no distinguishable bands.

6. *Tolane*, m. p. 60°. A medium continuous spectrum running from about 2915 to 4745 Å.U., fading off more gradually at the end of shorter wave-length. There are no distinguishable bands.

All the above spectra were obtained by an exposure of about 15 minutes on Eclipse plates with the drum-head of the slit at 20. The pressure was 1 mm. or less; and the temperature was sufficiently high to keep the substances vaporised at that pressure.

II. *Compounds containing Fused Rings*.

7. *Fluorene*, m. p. 112°. A very intense continuous spectrum running from 2900 to 4900 Å.U., with a diffuse band-head at 2990 Å.U.

8. *Acenaphthene*. Twice recrystallised from alcohol, this had m. p. 93·5°. Further recrystallisation made no change in the m. p. On visual observation, the discharge in the cell is pink in colour.

A very intense continuous spectrum running from about 2953 to 4650 Å.U., fading off gradually at both ends, with indications of diffuse heads of bands at 3064, 3172, 3207, 3353, and 3523 (?) Å.U. In the visible region, prolonged exposures with panchromatic plates revealed heads of bands at 5540, 5875, 6100, and 6370 Å.U.

9. *Anthracene*, purified by shaking with carbon disulphide, boiling with animal charcoal, and recrystallising; m. p. 216°. An extremely intense spectrum running from about 3240 to 5050 Å.U. with the most intense region between 3650 and 4450 Å.U. Diffuse heads of bands occur at 3247, 3414—44, 3462, 3617, 3642, 3688, 3820, 4055, and 4285 Å.U. The heads are very diffuse, so the foregoing readings are only approximate.

This anthracene spectrum is one of the most brilliant yet observed among the organic compounds. It was tested against an ordinary incandescent mantle at the same distance from the slit; and the two spectra were found to be of approximately the same intensity.

10. *Phenanthrene*, purified by dissolving 3 parts of phenanthrene in 5 parts of warm toluene; then cooling the solution to 10° and filtering to remove anthracene. The filtrate was evaporated until

all the toluene was expelled; and the process was repeated. Finally, the residue was twice recrystallised from alcohol; m. p. 96·2°.

An intense continuous spectrum running from 2960 to 4800 Å.U. the region 2960—3430 being weak and that at 3430—4800 being intense. Heads of bands occur at about 2971, 3430, 3635, 3682, 3819, and 4046. The heads of bands in this spectrum are not so intense as those in the anthracene spectrum.

11. *Naphthanthracene* (1 : 2-*benzanthracene*), m. p. 159°. A continuous spectrum from about 3360 to 4920 Å.U., fading off gradually at both ends and having a very intense region at 3810—4920 Å.U. Diffuse bands occur with heads at approximately 3500, 3635, and 3810 Å.U.

12. 1-*Methylnaphthalene*, b. p. 243·5—244·1°/763 mm. A very intense continuous spectrum running from about 3000 to 4500 Å.U., fading off gradually at both ends, with the most intense region between 3210—4000 Å.U. There are diffuse band-heads at 3115 and 3210, and a less distinct one at 3162 Å.U.

In the visible region, there are diffuse faint bands with heads at about 6020 and 6320 Å.U.

13. 2-*Methylnaphthalene*, m. p. 34°. A very intense continuous spectrum running from about 3000 to 4700, fading off gradually at both ends, with a distinct diffuse head at 3165 and possibly another head of a band at about 3310 Å.U.

There is also a region of emission in the visible, consisting of three bands with heads at (very approximately) 5890, 6030, and 6400 Å.U.

14. 9-*Phenylfluorene*, m. p. 145°, was prepared from triphenylchloromethane by Hemilian's method (*Ber.*, 1878, **11**, 837) and purified by recrystallising three times from glacial acetic acid and finally from alcohol.

An intense continuous spectrum running from about 2900 to 4200, fading off gradually at both ends, with a very indistinct band-head at about 3025 Å.U.

15. 9-*Phenylanthracene*, m. p. 156°.* A very intense continuous spectrum running from about 3550 to 4960 Å.U., fading off at both ends, with very indistinct broad bands of a diffuse character having heads approximately at 3770, 3930, 4155 Å.U.

These five substances—Nos. 11 to 15—gave very good spectra with an exposure of only a few seconds, say 15 seconds, so far as the ultra-violet region is concerned. The visible emission of the two methylnaphthalenes, however, requires an exposure of an hour

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* We wish to call attention to this m. p., which is that of a specimen kindly supplied by Mr. E. de Barry Barnett. The m. p. in the literature hitherto has been much lower—152—153°.

with a wide slit in order to produce a clear effect upon panchromatic plates.

16. $1:2:3:4:5:6:7:8$-*Octahydroanthracene*, m. p. 71·6°. A continuous spectrum of medium intensity extending from about 2835 to about 3800 Å.U., fading off more gradually towards the end of greater wave-lengths, with indications of very diffuse band-heads at about 2835, 2900, and 2940; this last one being the most distinct.

There is also a diffuse band in the green region, with its head at about 4860 Å.U.

To obtain a photograph showing this spectrum of medium intensity, an exposure of 15 minutes was necessary.

17. *Retene*, m. p. 97·5°, was obtained by two recrystallisations with the aid of animal charcoal.

A very intense continuous spectrum running from about 3250 to 4700 Å.U. and fading off gradually at both ends. No bands were detected.

III. *Discussion of the Results.*

(1) *Structural Separation of the Phenyl Groups.*—The influence of substitution on the benzene spectrum may be threefold, since it may affect (*a*) the number of the bands; (*b*) the total extension of the spectrum, and (*c*) the intensity of the spectrum. The following table (Table I) brings out the main changes in the case of the series : benzene, diphenyl, diphenylmethane, and dibenzyl, wherein the phenyl groups are being moved further away from each other in the structure.

TABLE I.

	Emission between.	Bands.	Intensity of spectrum.
Ph·H	2544—3450 (approx.)	78	Bright
Ph·Ph	2890—3900	2	Faint
Ph·CH₂Ph	2673—3900	2	Medium
Ph·CH₂·CH₂Ph	2700—4300	0	{ Faint between 2700 and 3390 { Bright between 3390 and 3950

The approximate extents of the various spectra are thus : Ph·H $=$ 900; Ph·Ph $= 1000$; Ph·CH₂Ph $= 1200$; Ph·CH₂·CH₂Ph $= 1600$ Å.U. The extension is mainly towards the red end of the spectrum, *i.e.*, it progressively includes slower and slower vibrations.

These facts show that the introduction of a second phenyl nucleus in direct attachment to the benzene ring produces a profound disturbance in the original benzenoid vibration; the regularity of the vibration is upset and the amplitude of the vibrations, as measured by the intensity, is reduced. When the second nucleus is separated from the other by a methylene group, the interference is less marked so far as amplitude of vibration is concerned. The diphenylmethane molecule shows no sign of returning to benzenoid regularity of vibration; instead, there is a steady progression of the

emission into the regions of longer wave-length, which suggests either a slowing down of the original vibration or else the production of fresh vibrations by interference.

The accumulation of three phenyl nuclei round a single carbon atom seems to intensify this process; since the triphenylmethane spectrum has a total extension of 1660 units and penetrates farther into the red end of the spectrum than any of the others mentioned above.

(2) *Fused Rings and Independent Nuclei.*—Table II brings into prominence the difference between the spectra of compounds containing two or more complete benzene rings and those of substances in which the six-membered rings have certain members in common, as in naphthalene.

TABLE II.

	Emission region.	Total extent.	Bands.
Diphenyl	2890—3900	1010	2
*Naphthalene	2800—5000	2200	2
Dibenzyl	2700—4300	1600	1
†Acenaphthene	2953—4650	1700	5
Triphenylmethane	2730—4390	1660	2
Anthracene	3240—5050	1810	9
9-Phenylanthracene	3550—4960	1410	3
1 : 2-Benzanthracene	3360—4920	1560	3

* J., 1923, **123**, 1745.

† Acenaphthene has also some bands in the visible region.

The foregoing figures bring out clearly that the fusion of two rings tends to produce a longer spectrum than that produced by the corresponding compound in which the rings have no common members. The intensity of the spectrum is also much greater in the case of the fused-ring compounds than in the analogous substances with independent rings.

Diphenylmethane and fluorene, and triphenylmethane and phenylfluorene might also be cited as examples of this type; but in these substances the ring-fusion produces a fresh cyclic grouping in the molecule. Substances of this nature will be considered in a later paper.

(3) *Conjugated Double Bonds.*—The Tesla-luminescence spectra seem to form an exception to the rule that conjugation has a marked effect upon optical properties. This marks out the Tesla-luminescence rather surprisingly; for the effect of conjugations has been traced in general absorptive power (Crymble, Stewart, Wright, Glendinning, and Rea, J., 1911, **99**, 451, 1262); in selective absorption (Stewart and Baly, J., 1906, **89**, 489); in refractivity (Bruhl, *Ber.*, 1907, **46**, 878, 1153; 1908, **47**, 3712); in magnetic rotation (Sir W. H. Perkin, J., 1906, **89**, 854; 1907, **91**, 806); and in optical rotatory power (Hilditch, J., 1908, **93**, 1388, 1618).

When the intensity of various spectra emitted by compounds containing conjugated chains is examined, the following results emerge.

TABLE III.

	Spectrum.	Bonds directly conjugated.
Diphenyl	Faint	6
Dibenzyl	Faint	3
Naphthalene	Bright	5
Triphenylmethane	Medium	3
Anthracene	Very intense	5
9-Phenylanthracene	Very intense	9
1 : 2-Benzanthracene	Very intense	10

Inspection will show that although in the main an increase in the length of the chain of conjugation seems to enhance the brightness of the spectrum, the first three spectra do not agree with this rule.

An interesting comparison is to be found in the cases of dibenzyl, stilbene, and azobenzene. The absorption spectra of these substances have been described by Crymble, Stewart, and Wright (Ber., 1910, 43, 1188). The absorption spectrum of dibenzyl contains a series of shallow bands between 3200 and 2400 Å.U. Instead of these, the stilbene spectrum has a single broad and deeply penetrating band covering the same region. The azobenzene spectrum, on the other hand, contains two bands : a broad band in almost the same region as the stilbene band (3450—2550 Å.U.); and a second band of much less penetration in the visible region, 5250—3800 Å.U., which is the origin of the red colour of the compound.

When the Tesla spectra of these three substances are examined, it is found that dibenzyl emits a faint spectrum in the region 2700—4300 Å.U.: stilbene shows an emission of medium intensity in the region 3100—4680 Å.U.; but azobenzene emits no vibrations whatever within the whole region of the photographic spectrum.

The difference between stilbene and dibenzyl might be ascribed to a difference in the length of the chain of conjugation in the molecule, the latter having three double bonds directly conjugated whilst stilbene has seven directly conjugated bonds. But this hypothesis fails to account for the fact that azobenzene with the same number of conjugated bonds as stilbene, and a molecular weight only two units higher, shows no emission whatever. Thus both in absorptive power and in the capacity of Tesla-emission, azobenzene differs from stilbene, although in structure the compounds are extremely similar. It appears that the group –N : N–, like the nitro-group and the chlorine atom, has the power of extinguishing Tesla-emission; and thus the closest resemblances in structure may be overborne by chemical factors.

(4) *Structural Isomerism.*—Both 1- and 2-methylnaphthalene give intense continuous spectra beginning at approximately 3000 Å.U., but whilst the emission of the 1-methyl compound stops at 4500 Å.U., that of the 2-methyl derivative extends up to 4700 Å.U. There is a difference in the positions of the diffuse band-heads in the two spectra also. This shows that even a slight structural difference has its effect upon the nature of the Tesla-spectra.

With deeper alterations in structure, the differences between the spectra of isomerides become more marked, as can be seen from the following figures relating to three compounds with the formula $C_{14}H_{10}$.

TABLE IV.

	Emission.	Region of emission.	Bands.
Tolane	Faint	2915—4745	0
Phenanthrene	Intense	2960—4800	6
Anthracene	Very intense	3240—5050	9

Thus the spectrum is faint when the atoms are grouped in separate nuclei and becomes more intense as the rings are fused into a connected structure. Simultaneously there is a shift of the spectrum towards the red and an increase in the number of bands.

(5) *The Introduction of Substituent Groups.*—Apparently the mode of linking governs the effect of an entering phenyl radical upon the spectra. When the phenyl group is attached to an aliphatic carbon atom, its effect appears to be twofold : it increases the length and diminishes the intensity of the spectrum.

TABLE V.

Aliphatic linking.

	Extent of spectrum.	Intensity.
$Ph \cdot CH_3$	2602—3700	Intense spectrum
$Ph \cdot CH_2Ph$	2763—3900	Strong medium spectrum
$Ph \cdot CHPh_2$	2730—4390	Weak medium spectrum

Similar results are found in the cases of ethylbenzene and dibenzyl; styrene and stilbene; phenylacetylene and tolane.

On the other hand, when a phenyl nucleus is directly attached to *the ring* of a parent compound, the spectrum is shortened and the intensity is, if anything, increased.

TABLE VI.

Phenyl attached directly to ring.

	Extent of spectrum.		Extent of spectrum.
Fluorene	2900—4900	Anthracene	3240—5050
9-Phenylfluorene	2900—4200	9-Phenylanthracene	3550—4960

The introduction of alkyl substituents in the case of fused-ring compounds appears to lead to a shortening of the spectrum, as can be seen from the following figures :

	Extent of spectrum.		Extent of spectrum.
Naphthalene	2800—5000	Naphthalene	2800—5000
1-Methylnaphthalene	3000—4500	Acenaphthene	2953—4650
2-Methylnaphthalene	3000—4700	Phenanthrene	2960—4800
		Retene	3250—4700

IV. *The Sensitiveness of the Tesla Spectra.*

In the course of the present work, an opportunity was accidentally given to test the value of the Tesla-spectra as a means of detecting impurities in the substance under examination. A sample of triphenylmethane obtained through the ordinary trade channels was purified by recrystallisation in the usual manner and was then photographed. Inspection of the photograph showed that the spectrum consisted of two parts : a long faint section beginning about 2700 and merging sharply into a very much brighter band in the region of 3600 Å.U. The position and brilliancy of the latter section suggested that it might arise from a trace of anthracene which still remained in the " triphenylmethane " sample even after ordinary purification. The percentage of anthracene impurity was extremely small, too minute to be detectable by means of the melting point. But by repeated recrystallisation from alcohol the impurity was removed; and the final product gave the true triphenylmethane spectrum, which has no bright band in it at all. Thus the Tesla-spectrum can be used to detect the presence of minute quantities of certain impurities.

It may be mentioned that Baker (J., 1907, **91**, 1494) had a similar experience when examining the absorption spectrum of triphenylmethane. His original sample was contaminated with anthracene, *inter alia,* which is evidently formed as a by-product in the Friedel–Crafts synthesis of triphenylmethane from benzene and chloroform.

CXXXVIII.—*The Mechanism of the Formation of Malachite from Basic Cupric Carbonate.*

By JACK REGINALD IRONS HEPBURN.

THIS paper details the results of an investigation into the mode of formation of the crystalline basic cupric carbonate, malachite, from amorphous basic cupric carbonate.

I. *Formation of Malachite in the Cold by Prolonged Keeping.*

Pickering (J., 1909, 95, 1409) has shown that by intermixture of a cupric salt and a soluble carbonate a voluminous colloidal-amorphous precipitate, having the composition $5CuO,2CO_2$ at the moment of its formation, is produced which, after a few days' contact with the mother-liquor, changes in appearance and colour with production of the stable basic cupric carbonate, malachite $(2CuO,CO_2)$.

A series of systematic experiments was made on the influence of dilution and proportion of reagents upon this transformation.

The experiments were carried out with solutions of sodium carbonate and cupric sulphate varying in concentration from saturated to $N/40$. The volume was adjusted in each case so that the amount of precipitate was equivalent to that obtained by intermixture of 25 c.c. of N-reagents. This method follows that of v. Weimarn ("Zustande der Materie," 1914, p. 4) which was employed by him in another connexion.

Preliminary experiments on the initial precipitation with concentrations increasing from $N/200$ showed that within this concentration range the initial precipitate retained the same microscopic form.

The experimental details are summarised in Table I.

TABLE I.

Experiment No.	Strengths of solutions.	C.c. of Na_2CO_3.	C.c. of $CuSO_4$.	Malachite formed after (days).	Experiment No.	Strengths of solutions.	C.c. of Na_2CO_3.	C.c. of $CuSO_4$.	Malachite formed after (days).
I	$N/40$	1000	1000	18	VII	$N/2$	50	50	3
II	$N/40$	1400	1000	13	VIII	$N/2$	80	50	7
III	$N/20$	500	500	10	IX	N	25	25	2
IV	$N/20$	800	500	9	X	N	40	25	6
V	$N/10$	250	250	4	XI	$N/10$	250	250	30
VI	$N/10$	400	250	8				+ 5 c.c. of 20% gelatin.	

The times given are approximate only, and indicate periods after which the microscopic appearance showed no further change.

In Expt. V the initial products of the precipitation were the basic carbonate, sodium sulphate, and carbonic acid. When the

precipitate from $N/10$-solution was washed free from all adhering reagents and suspended in water free from carbon dioxide, the transformation was completely inhibited. But the change to malachite was accomplished when the well-washed colloidal precipitate was suspended in an aqueous solution of carbon dioxide.

In Expt. VI the initial products of the precipitation were the basic carbonate, sodium sulphate, and sodium hydrogen carbonate. The metamorphosis in this case was brought about through the agency of the sodium hydrogen carbonate, a fact which was demonstrated directly by the occurrence of the same change on suspending the well-washed basic carbonate in sodium hydrogen carbonate solution of the same concentration.

Experiment XI consisted in the repetition of Experiment V in the presence of 0·2% of gelatin. The change was considerably retarded, but was otherwise unaltered, malachite again being the final product. Mond and Heberlein's statement (J., 1919, **105**, 908) that a small amount of gelatin (0·1%) stabilised the precipitate, does not appear to be confirmed by this result.

When the basic carbonate was suspended in $N/10$-sodium carbonate solution, blackening ensued after 3 days with loss of carbon dioxide and formation of sodium hydrogen carbonate. A similar result was obtained by Pickering (*loc. cit.*), both results being contrary to Mond and Heberlein's statement (*loc. cit.*) that in the presence of sodium carbonate solution the amorphous precipitate was stable.

The course of the change in every case above was followed by microscopic observations.

Freshly precipitated basic cupric carbonate (over a range of concentration from $N/200$ to $3N$) consisted of a hydrogel and appeared under the microscope as ill-defined aggregates of gelatinous highly-hydrated material of low refractive index, and absolutely opaque in polarised light.

Sharply-defined changes of a similar nature were observed in all concentrations lower than $N/10$, after allowing the precipitate to stand. With the stronger solutions the changes were not so well marked. The formation of malachite with $N/10$-reagents (Expt. V) was of especial interest. After 4 days' standing, a drop of liquid containing the product in suspension was examined under the microscope. The product was evidently crystalline and consisted of green and blue sphærocrystals ($d = 100\mu$). After 10 days' standing, a further profound change had occurred, with production of sharp excrescences over the surface of each sphærocrystal. The final product consisted of normal malachite crystals which reacted brilliantly in polarised light (Fig. 1. × 240).

FIG. 1.—*Normal malachite* (× 240).
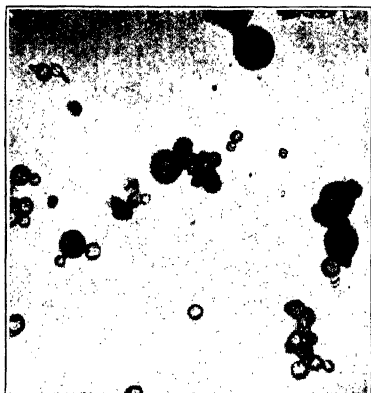
FIG. 2.—*Sphærocrystalline malachite* (× 240).

FIG. 3.—*Film of malachite* (× 240).
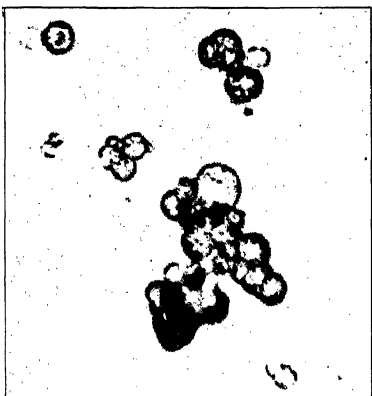
FIG. 4.—*Sphærocrystalline malachite* (× 480).
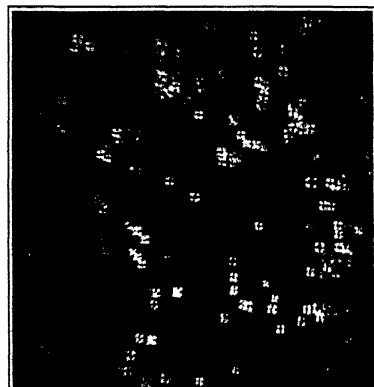
FIG. 5.—*Sphærocrystalline malachite*
(*polarised light*) (× 240).
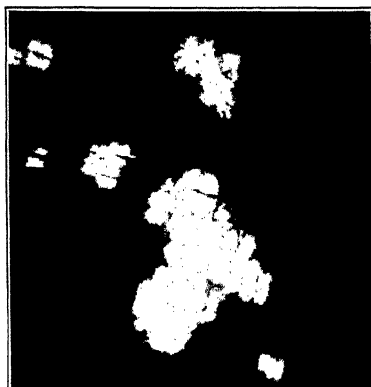
FIG. 6.—*Sphærocrystalline malachite*
(*polarised light*) (× 480).

In Experiment VI, after 6 days' standing, microscopic examination revealed the presence of minute spheres embedded in the gelatinous masses. Regular growth continued within the hydrogel, and the final product presented the appearance shown in Fig. 2 ($\times$ 240) and consisted of malachite sphærocrystals, some of great structural beauty, and reacting normally to polarised light.

Similar, but less rapid changes occurred with the more dilute reagents. With N-reagents, the sphærocrystals were very much smaller in size, imperfect in formation, and aggregated.

II. *Formation of Malachite from Hot Solutions.*

A modification of Field's method was used (J., 1862, **14**, 70).

Saturated cupric sulphate solution was added from a burette to 50 c.c. of a freshly-prepared saturated solution of sodium hydrogen carbonate with violent agitation, in the cold, until the precipitate no longer redissolved. A further equal volume of cupric sulphate was added, and the whole rapidly heated at 100°. After a few minutes, the deep blue solution suddenly decolorised, and a green, lustrous film, consisting of malachite, formed on the walls of the vessel. The film was readily detached and disintegrated by further boiling.

In the presence of the normal carbonate, malachite was not precipitated at 100°, but a black powder containing less carbonic acid was formed as a similar film. A similar effect was observed if the sodium hydrogen carbonate solution was not freshly prepared. This action was subsequently shown to be due to the presence of the normal carbonate.

If the basic carbonate initially precipitated remained partially undissolved on heating at 100°, it was converted directly into malachite without intermediate film formation.

In the presence of 0·5% of gelatin, the blue solution gave the same products; the reaction, however, was greatly retarded, and occupied 30 minutes instead of from 2 to 3 minutes.

Microscopic observation showed the film of malachite to consist of what may be termed colonies of embryo sphærocrystals (Fig. 3. $\times$ 240). The individual sphærocrystals were very uniform in size, and the film reacted to polarised light. After the solution had been boiled for a short time, the film disintegrated into individual sphærocrystals and larger aggregates. Many of the larger spheres showed well-marked zonal structure. When formed without intermediate film formation (Fig. 4. $\times$ 480), the malachite consisted of small and poorly developed sphærocrystals, generally aggregated in clusters.

Some light may be thrown on the cause of the origin of sphærocrystals by the following considerations. Applebey and Lane (J.,

1918, 114, 609) have suggested that the blue solution contains a suspensoid (basic cupric carbonate or a double sodium cupric carbonate); the evidence brought forward in support of this assumption, however, seems somewhat inadequate, and appears to rest on the observation that addition of a large amount of sodium phosphate precipitated the blue salt. Further evidence in favour of the view that a suspensoid is present in the blue solution is found in the fact that such solutions show a well-marked Tyndall cone in which the light scattered at right angles to the entrant beam is plane polarised. The assumption of the presence of a suspensoid is in accordance with the intense colour of these solutions (compare Applebey and Lane, *loc. cit.*, p. 620); further, Bradford (*Biochem. J.*, 1918, 12, 357) has suggested—in another connexion— that sphærocrystals are the products of coagulation of aggregated particles of colloid dimensions. Hence it seems possible that malachite sphærocrystals may be produced, with intermediate film formation, through coagulation of the colloid by heat. In this case the function of gelatin in retarding this change would be that of a normal protective colloid and would be analogous to its action in stabilising solutions of colloidal gold.

Morphological and Optical Properties of Malachite Sphærocrystals.

Following the method described above, malachite may be prepared in quantity in the form of sphærocrystals of uniform size.

Size of Particles.—This was determined by two independent methods.

I. *By the scale micrometer.* A scale micrometer standardised against a Zeiss stage micrometer (graduated to 1/100 mm.) was employed, with $\frac{1}{6}$-inch objective. From several observations the mean diameter was found to be 6 μ.

II. *By halo production.* A similar method for the average diameter of a group of particles of uniform size has been employed by Young (*Ann. Philos.*, 1813, 2, 115) and elaborated by Quincke (*Ann. Physik*, 1902, 7, 734).

The source of illumination employed was a single straight-filament carbon lamp, which was viewed through the malachite slide together with a green glass, in the first experiment, and a red glass in the second. The prominent wave-length of the light transmitted was determined from observations with the spectrometer (for green glass = 0·00053 mm.; red glass = 0·00064 mm.).

From the width (*b* cm.) of the halo the diameter of the particles (*d* mm.) was calculated according to the formula

$$d = \lambda Eb,$$

where λ = wave-length of light used (mm.) and E = distance between the source of illumination and the slide (cm.).

For green light b was found to be 14 cm., and for red light, 17 cm. Each of these values gives $d = 6\mu$.

The result is in agreement with that obtained by direct microscopic observation. This method seems well adapted for the determination of the average diameter of particles of uniform size.

Density.—It has been suggested that sphærocrystals are closely allied in nature to colloid substances under strain (Quincke, *loc. cit.*; Bradford, *loc. cit.*), in which case the density of the sphærocrystalline modification of a substance would probably differ from that of the normal crystalline form. The suggestions above were put to the test by determinations of the density of sphærocrystalline malachite. Using the specific gravity bottle, the result obtained was 3·64 (mean of two concordant determinations).

This result is slightly lower than that for natural malachite (d 3·7 to 4·0). However, it would not appear justifiable to draw definite conclusions from such small variations.

The value obtained above was confirmed by observations of the rate of fall of the particles in a cloud. A suspension of malachite was prepared in air-free distilled water, and allowed to subside in a tube of small cross-section.

The rate of fall (v) was $4\cdot3 \times 10^{-3}$ cm. per sec., which gave a value of 3·6 for the density, d, as calculated from the ordinary formula

$$d - D = 9\eta v/2r^2 g,$$

where D is the density of water and the other letters have the usual significance.

The difference in the density of individual sphærocrystals was also investigated by observation of the rate of transit across the microscopic field, using a $\frac{1}{4}$-inch objective and capillary tube.

The apparent diameter of the field was 3·50 mm. The variation in the times of transit of individual particles was small and the average time of transit, 77 seconds. From the average observation, the density was found to be 3·7.

Optical Properties.—The sphærocrystals of malachite, when viewed with crossed nicol prisms, showed a characteristic interference pattern, photographs of which are shown in Figs. 5 ($\times$ 240) and 6 ($\times$ 480). The pattern consisted of a dark cross with four bright sectors, surrounded under certain conditions by colour rings. The same reaction is shown by circular particles of amorphous substances under strain. This provides a means of testing the assumption of crystallinity in the malachite spherites. Spherites of amorphous substances under strain, together with those of uniaxial

crystalline substances (*i.e.* belonging to the tetragonal, hexagonal or orthorhombic system) exhibit a shadow cross with the arms accurately at right angles (Rosenbusch, *Mikroscopische Physiographie*, 1904, **1**, 395). The pattern observed is identical with that produced by convergent polarised light impinging upon a thin plate of a uniaxial crystal (compare Tutton, "Crystallography," 1911, p. 670). Spherites of biaxial crystalline substances (*i.e.*, belonging to the monoclinic or triclinic system), on the other hand, show shadow crosses, the arms of which are not accurately at right angles, the pattern produced being closely analogous to that shown by biaxial crystalline plates in convergent polarised light. An examination of Figs. 5 and 6 reveals that the pattern shown is a biaxial one, certain particles exhibiting the characteristic design seen on rotating a biaxial crystalline plate in convergent polarised light. They are clearly not amorphous substances under strain. This observation is in agreement with the fact that naturally occurring normal malachite crystals are optically biaxial and belong to the monoclinic system (Dana, "Mineralogy," 1899, p. 295).

Summary.

The course of the changes which occur in the transformation of the unstable amorphous cupric carbonate into the stable crystalline substance, malachite, has been followed by direct microscopic observation throughout a wide range of concentrations, at the ordinary temperature and at 100°.

Transformation in the cold appears to be brought about through the intermediate agency of an aqueous solution of carbon dioxide or sodium hydrogen carbonate. In the presence of a solution of carbon dioxide, the resulting malachite consists of normal crystals. When the change is brought about by sodium hydrogen carbonate, the product consists entirely of malachite sphærocrystals. These are probably produced through crystal growth in a colloid medium (*viz.*, the unchanged basic cupric carbonate). In the presence of gelatin the change is considerably retarded, but is unaltered both in character and in products. When malachite is formed at 100° by thermal decomposition of the blue solutions prepared by dissolving the basic carbonate in saturated sodium hydrogen carbonate solution, the product (in the absence of foreign nuclei) consists of a surface film of interpenetrating sphærocrystals. The film is disrupted into individual sphærocrystals by further boiling. The direct cause of the change is to be attributed to loss of carbon dioxide from the sodium hydrogen carbonate at 100° with formation of the stable double salt $Na_2CO_3,NaHCO_3,2H_2O$ (Habermann and Kurtenacki, *Z. anorg. Chem.*, 1909, **63**, 65) and malachite.

Gelatin similarly retards this change.

As far as a search of the literature has been made, this records one of the first cases in which sphærocrystals form the sole product of a normal chemical reaction.

CXXXIX.—*Periodic Electrochemical Phenomena.*

By ERNEST SYDNEY HEDGES and JAMES ECKERSLEY MYERS.

IN continuation of the work being developed in this laboratory on the principle of periodicity in chemistry, some of the periodic reactions previously described (J., 1924, **125**, 604, 1282; this vol., p. 445) have been examined from the electrochemical standpoint. This method not only furnishes a delicate means of following the course of reactions where the rate of evolution of gas is so slow as to render the manometric method inapplicable, but also provides data which are of importance in the elucidation of the mechanism involved in the periodic dissolution of metals. Further, it would seem that the method has a considerably wider scope, being adapted in particular to the case of reactions involving the deposition of metals, and it is intended to continue investigations in this direction.

There are scattered throughout the literature several reported cases of periodic electrochemical phenomena, and as consideration of these is important not only in their bearing on the work described here, but is also essential to the correct presentation of periodicity as a principle, a brief account is given of the results of previous investigators. The work may be considered in two sections : (*a*) where current is taken from the system, (*b*) where current is led into the system.

Section (*a*).—Early cases of such periodicity concerning an iron electrode are mentioned by Fechner (*Schweigg. Journ.*, 1828, **53**, 141) and by Schönbein (*Pogg. Ann.*, 1836, **38**, 444). Kistiakowsky ("Nernst-Festschrift, Knapps Verlag.," Halle-a.-S., 1912) obtained a periodic current from the cell—Fe(rusted)|5%$K_2Cr_2O_7$,N-H_2SO_4|Fe (periodic)—in which the electrode responsible for the periodicity consisted of the purest iron, scrupulously cleaned and then immersed in 10% sulphuric acid before the experiment. By employing two electrodes of similarly treated iron in the same solution, he suc-

ceeded in making a cell which produced an alternating current— the two electrodes periodically reversing in polarity (*Z. Elektrochem.*, 1909, **15**, 268). It is interesting to observe that in this case the metal requires a quite definite form of treatment or activation. Kistiakovski also found (7th Intern. Congr. Appl. Chem., 1909, Sect. 10, 56) that iron becomes alternately active and passive in dilute nitric acid, chromic acid, or potassium permanganate solution.

Brauer (*Z. physikal. Chem.*, 1901, **38**, 441) obtained a fluctuating difference of potential between Ostwald's chromium and the solution in which it dissolved, and Antropoff (*ibid.*, 1908, **62**, 513) found the potential difference between mercury and hydrogen peroxide to vary periodically, synchronising with the periodic evolution of gas. Heyrovský (J., 1920, **117**, 28) describes sudden changes and fluctuations between the values 0·77 and 1·67 volts for the E.M.F. of the cell Hg|Hg₂Cl₂,*N*-KCl|Al. This is precisely similar to the periodic dissolution of aluminium amalgam in hydrochloric acid described by the present authors (*loc. cit.*, p. 622).

Section (*b*).—Periodic fluctuations in current were observed by Schönbein (*Archives de l'Electricité*, 1842, **2**, 269) in leading a current through the cell $\overset{+}{\text{Fe}}$|dil.H₂SO₄|Pt, and by Joule (*Phil. Mag.*, 1844, **24**, 106) when a potential difference of 3·3 volts was applied to the cell $\overset{+}{\text{Fe}}$|H₂SO₄|$\overset{-}{\text{Zn}}$ amalgam. There were corresponding periods of dissolution of iron and evolution of oxygen at the anode. Heathcote (*Z. physikal. Chem.*, 1901, **37**, 368) states that when a current was passed through the cell $\overset{-}{\text{Pt}}$|HNO₃(*d* 1·4)|$\overset{+}{\text{Fe}}$, the needle of an ammeter placed in series exhibited regular oscillations. Different results were obtained with different pieces of iron and it may be observed that in many of these cases the influence of minute traces of impurities is not excluded, and the effect may be due—as in Ostwald's experiment with chromium—to an activating agent already present in the metal. Fredenhagen (*Z. physikal. Chem.*, 1903, **43**, 1) electrolysed sulphuric acid with an iron anode and obtained a periodic current after addition of chlorine ions. This result may be compared with the experiments of the present authors (experimental portion of this paper) on the deposition of iron on magnesium from solutions in sulphuric acid (non-periodic) and hydrochloric acid (periodic).

Adler (*Z. physikal. Chem.*, 1912, **80**, 385) extended Joule's experiments on the periodic electrolytic dissolution of iron and studied the effect of varying current density and other conditions of experiment. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 807; *Versl. Kon. Akad. Wetensch. Amsterdam*, 1915, **24**, 745;

1918, **27**, 159) found that with certain current densities an iron electrode immersed in a solution containing a mixture of ferrous sulphate and ferrous chloride gave a potential rapidly alternating from a positive to a negative value with an amplitude of 1·74 volts. He explains this as due to the periodic acceleration of establishment of inner equilibrium in the metal by the chlorine ions, but admits that this cannot explain Adler's results.

Another instance of periodic electrolytic phenomena occurring at the anode is given by Müller (*Z. Elektrochem.*, 1904, **10**, 519), who observed pulsations in the E.M.F. of a manganese electrode dissolving in faintly acid sodium phosphate solution. Byers observed a similar effect (*J. Amer. Chem. Soc.*, 1908, **30**, 1729), using a cobalt anode in sodium sulphate solution. Liebreich (*Z. Elektrochem.*, 1921, **27**, 94; compare also Kleffner, *ibid.*, 1923, **29**, 448) describes periodic phenomena in the electrolysis of chromic acid. Kohlrausch reports (*Physikal. Z.*, 1900, **1**, 88) that, when electrolysing platinum tetrachloride for the purpose of preparing pure platinum, he had once obtained a periodic evolution of gas, but subsequent attempts to repeat this had proved unsuccessful.

Periodic changes in anodic potential and in current density were observed by Küster (*Z. anorg. Chem.*, 1905, **46**, 113) and by Köhlichen (*Z. Elektrochem.*, 1901, **7**, 629) during the electrolysis of sodium sulphide solution with platinum electrodes. There was a corresponding periodic formation and dissolution of a film of sulphur over the anode surface. The chief factors in the production of waves were found to be the *size, position, and nature of surface* of the platinum electrodes. In general, the phenomenon did not occur at all when bright platinum foil was used, and a rough surface was found to answer best. These facts find a ready explanation in the light of the experiments of the present authors concerning the activation of metals. In all probability, the periods were only obtained when the platinum was in the active state. Kremann and Schoulz (*Monatsh.*, 1912, **33**, 1291) observed a similar periodicity in the electrolysis of alkali iodides between platinum electrodes. Examples are given of irregular waves resembling those often obtained by the present writers when the activating agent has been a metal. Windelschmidt (*Diss.*, Münster, 1907) and Dietrich (*Diss.*, Münster, 1910) obtained a periodic current in the electrolysis of ammoniacal solutions of nickel salts.

Several cases are also on record of periodic electrochemical phenomena occurring at the cathode. Förster (*Z. Elektrochem.*, 1902, **8**, 500) found the deposition of copper from a strongly acid solution of the nitrate to be periodic at high current densities, and a similar case is quoted by Cohen (*ibid.*, p. 499) in electro-

lysing an acid solution of bismuth nitrate.   Kremann and Suchy (*Wiener Sitz.*, April, 1913) found a periodically changing cathode potential in the deposition of a 50% iron–nickel alloy from a mixture of the sulphates.   Coehn (*Z. Elektrochem.*, 1901, **7**, 633) electrolysed a solution of an alkali salt with a mercury cathode and noticed that the surface of the mercury alternately became grey and then bright, whilst hydrogen was evolved during the bright periods. The course of the phenomenon was registered photographically by Kremann and Lorbeer (*Wiener Sitz.*, April, 1913).   Mercury is the one metal which the present authors believe to be normally periodically active.   Haber (*Z. Elektrochem.*, 1901, **7**, 634) observed periods in the electrolytic reduction of nitrobenzene in alcoholic solution at a platinum cathode.

It is relevant to mention the pulsations of the mercury surface observed by Roshdestwensky and Lewis (*Trans. Faraday Soc.*, 1912, **8**, 220) when mercuric cyanide was used in a capillary electrometer.

<div align="center">E X P E R I M E N T A L.</div>

The Apparatus.—The measurements of potential were made with a Dolezalek quadrant electrometer, the needle of which was charged to 90 volts by means of a battery of dry cells.   The system consisted of one or more metal electrodes immersed in the appropriate solution contained in a glass bottle of 100 c.c. capacity, which was fitted with a wide rubber stopper carrying glass tubes through which the electrodes were sealed.   The reading scale was so placed that one volt gave a deflection of 273 divisions (mm.).   By means of a bridge of saturated potassium chloride solution leading to an auxiliary saturated calomel electrode, it was possible to determine the potential difference between the two metal electrodes immersed in the solution or between each metal and the standard reference electrode.   In either case, one electrode was earthed and the other connected to one pair of quadrants of the electrometer, the other pair also being earthed.   The method of suspension of the metal electrodes was found to be of importance and in the first experiments, where the metals were suspended from platinum hooks sealed into glass tubes, constant results were not always obtained.   The difficulty was overcome by fastening the metals to a stout platinum rod with the aid of a platinum screw.   The rod was soldered to copper wire and sealed into glass by means of wax.

In later experiments, in order to compare the chemical and electrical effects, the apparatus was combined with that described by the authors in a previous paper (*loc. cit.*), the course of the reactions being recorded simultaneously on the electrometer scale and on the manometer.   The two sets of curves agree very closely

when the frequency and amplitude of the oscillations are not great, but in order to register the short waves electrically it would be necesary to use a more dead-beat instrument. The natural period of the electrometer needle suspended as in these experiments was 16 seconds. Simultaneous readings of potential and of gas pressure were taken every 30 seconds and the potentials recorded

GRAPH 12.

Mg-Ni Electrode in 0·3 N·HCl

GRAPH 13.

Mg and Cu in contact in 0·3 N·HCl
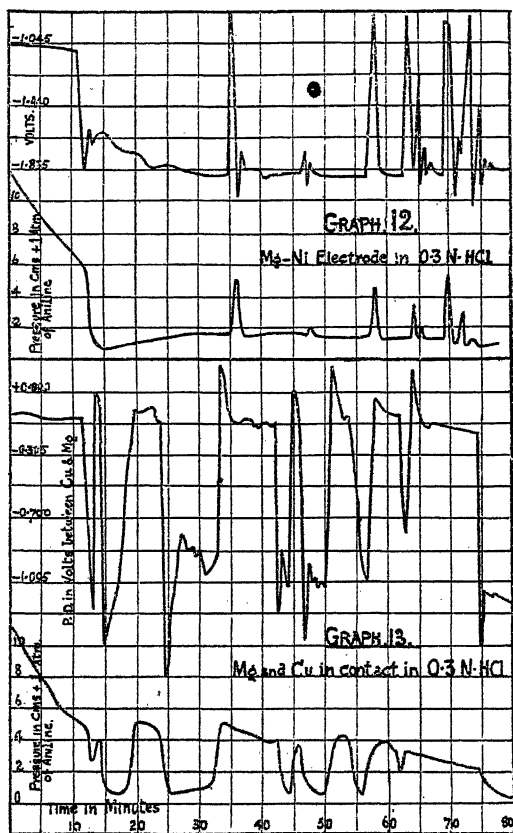
are expressed with reference to the saturated calomel electrode. All the experiments were carried out at room temperature.

Examination of some Metal Systems.

The authors have already shown (loc. cit.) that certain metallic couples dissolve in acids in a periodic manner after the second metallic component (i.e., the cathodic metal which does not dissolve) has been treated or "activated" by certain processes. Graph 12 represents the potential against the saturated calomel

electrode acquired by such a couple of magnesium and nickel sheet dissolving in 0·3N-hydrochloric acid, and below is plotted the synchronous variation in gas pressure. The periods are not very regular, but this is often a feature of systems where the activating agent is a second metallic component, and in a former communication (this vol., p. 445) a study was made of the conditions necessary to ensure regularity of wave form.

Simultaneous periodic curves of this type have been obtained with couples of magnesium with platinum, gold, cobalt, and copper in ammonium chloride solution, and with aluminium amalgam in hydrochloric acid. In the example illustrated in the graph, and in many of the other instances mentioned, the periodic nature of the evolution of gas was easily visible to the eye. It appeared that during the periods of high gas pressure the excess of hydrogen came from the nickel or other cathodic metal, the dissolving magnesium preserving at all times a slow and apparently steady rate of evolution of gas. This is quite in accordance with other experiments which indicate that the seat of the periodicity is the second metallic component.

In Graph 13 is recorded the periodic potential difference existing between electrodes of magnesium and activated copper in contact immersed in 0·03N-hydrochloric acid. Comparison of this with the foregoing graph shows that the periodic evolution of hydrogen is attended by simultaneous variations in (a) the potential of the couple as a whole with respect to the solution and (b) the potential difference between the two components. In the latter case, the copper appeared to be quite inert so long as the high potential difference lasted, and when the potentials of the two metals approached each other hydrogen was evolved from the surface of the copper. In the case of magnesium couples, another easily visible indication of the periodicity is to be observed in the behaviour of a dark grey oxide film which appears on the magnesium. This film forms even in acid solution at the point of contact of the two metals and extends for the distance of a millimetre or two. During the periods of strong gas evolution, the film begins to spread and may grow to a length of 1 or 2 cm. When the next slow rate of evolution commences, the film dissolves gradually, but not completely. The formation or dissolution of this oxide film has been observed always to follow and never to precede the change in potential of the couple. The authors therefore regard its appearance as a concomitant effect of the inherent periodicity rather than as a cause of the phenomenon, as in the case of the periodic mercury–hydrogen peroxide catalysis (loc. cit., p. 1283).

Periods have not been obtained, in experiments with platinum,

gold, silver, and nickel as activating agents, when the cathodic and dissolving metals were not in contact. Some contradictory results obtained, with copper, were probably due to the slow dissolution of this metal, which is known to take place in hydrochloric acid, followed by reduction at the surface of the magnesium.

Effect of Activation on the Potential of Metals.

It is well known that the condition of the surface of a metal has a considerable influence on the potential it acquires, and experiments by Vieweg (Ann. Physik, 1924, 74, 146) show that the contact potentials, measured against a standard metal, of aluminium, copper, nickel, gold, and platinum are affected by heating in a vacuum in a similar way to the change produced by mechanical cleaning of the surface. It has now been found that the value for the metal after treatment differs considerably from that of the inactive metal. The change is in the negative direction in the cases of copper and silver, and positive in the case of platinum and of gold. The potential of ordinary copper foil in $0.3N$-hydrochloric acid against the saturated calomel electrode was determined as -0.11 volt and the values -0.26, -0.19, -0.22 volt were obtained with different specimens of the active metal after scraping. A sample of copper after vacuum-heat treatment registered a potential of -0.18 volt. A silver electrode after vacuum-heat treatment changed its potential in N-hydrochloric acid by 0.03 volt in the negative direction. Gold in $0.1N$-hydrochloric acid gave an initial value of $+0.17$ volt, changing, after vacuum-heat treatment, to $+0.25$ volt. Platinum (platinised) in N-hydrochloric acid registered a potential of $+0.19$ volt, which became $+0.38$ volt after treatment. The difference is not so great as that brought about by depositing platinum black on a platinum surface. The potential of a piece of bright platinum foil in $0.1N$-hydrochloric acid was $+0.19$ volt, and this became $+0.48$ volt after platinising from a solution of chloroplatinic acid. After keeping for 3 days, this high value sank to $+0.41$ volt. The potentials of activated metals gradually return to the normal value on keeping, corresponding with the previously described dying of the activity.

Another factor entering into the consideration of the potentials assumed by activated metals during the reactions is the influence of the hydrogen with which the solution soon becomes saturated and which is absorbed by the metal. The effect of this is to make the metal more negative, but on standing for an hour there is a partial return to the former value. In the case of activated copper, the effect due to the hydrogen is complicated by the partial return

of the metal to the inactive state—a factor operating in the reverse direction. Graph 14 conveys a clear impression of how the dissolution of magnesium in $0.3N$-hydrochloric acid is affected by contact with activated and with inactive platinum, both from the electrical and from the chemical point of view.

Some Reactions involving the Deposition of Metals.

When magnesium dissolves in dilute hydrochloric acid containing ferrous sulphate in solution, reduction takes place and iron is deposited as a black film on the surface of the magnesium. By suitably choosing the concentration of the reagents, periodic phenomena may be observed in this reaction. This particular case was first found by the visible periodic changes which occur in the system; in fact, the system itself serves admirably as an optical demonstration of chemical periodicity. After an initial lapse of time dependent on the relative concentrations of the reagents, a film of reduced metal spreads from one or two centres on the magnesium surface until it covers about half the metal electrode. Then it proceeds to dissolve, leaving the electrode with a bright surface. The black film grows a second time, covering a greater surface of electrode, and then redissolves, leaving a few black patches on the magnesium.
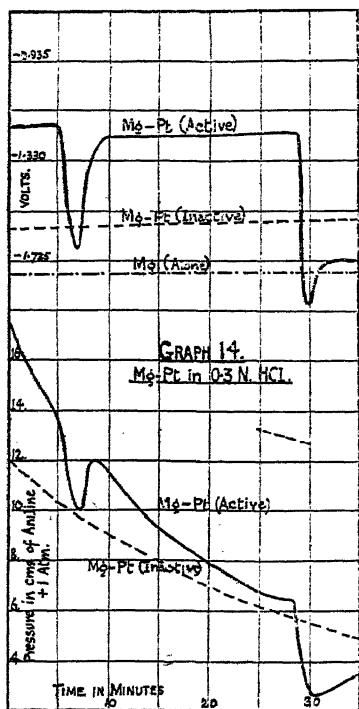
These two processes continue in alternation a number of times and in each successive period both the area covered by the growing film and the area of the film remaining after the partial dissolution increase. This continues until finally the film, even in its partially dissolved state, entirely covers the electrode. There is no reason to suppose that the periodic phenomenon is then at an end. It is probable that the film continues to grow periodically in thickness as it can no longer do so in extent, and when the surface is once complete no further change in the potential is to be expected. Hydrogen is evolved throughout.

The change has been followed in the apparatus described, simultaneous observations being made of the potential of the dissolving metal, the pressure of the evolved hydrogen, and the appearance of the film. The electrical change synchronised exactly with the chemical change indicated by the appearance of the film. The potential of the magnesium became more positive as its surface was covered by the growing film of iron and returned in the negative direction as the surface brightened through dissolution of the film.

The mean amplitude was in most experiments about 0·03 volt. The amplitude of the oscillations decreased throughout the experiment consistently with the relative areas covered by the film at the maxima and minima of successive waves. The rate of evolution of hydrogen remained steady throughout. The frequency of the oscillations increased with the concentration of ferrous sulphate and was independent (between the limits 0·6N and 0·2N) of the concentration of acid. The authors have found (*loc. cit.*, 1924, p. 611; this vol., p. 447) that the frequency of other periodic reactions is proportional to the concentration of reagent and *decreases* with increasing amount of activating agent. The hydrochloric acid and the ferrous sulphate are not to be regarded, therefore, as reagent and activating agent respectively, but rather the ferrous sulphate is the reagent and the reduced iron is an active second metallic component. This is also consistent with the absence of periodicity in the rate of evolution of hydrogen. Experiments in which the solution was vigorously stirred by means of an air blast showed that the phenomena were not affected thereby in any way. This removes any possibility of a periodic diffusion of the reactants or reaction products.

Graph 15 represents some of the experiments which have been carried out on this system, and shows the effect of varying the concentration of ferrous sulphate between the limits 0·01% and 0·05% of $FeSO_4,7H_2O$, the hydrochloric acid being kept at 0·3N strength. In these curves, the first reading was taken 3 minutes after the commencement of the experiment, in order to eliminate the initial vigorous swinging of the electrometer needle. In an experiment in 0·3N-hydrochloric acid with addition of 0·1% of crystallised ferrous sulphate, the periodic film formation was observed during the first 3 minutes, after which the permanent deposit set in, so that electrical measurements could not be taken. It is probable that in stronger solutions, where the deposition takes place immediately on immersing the metal, very rapid oscillations incapable at present of detection are actually existent.

When the hydrochloric acid was replaced by 0·3N-sulphuric

acid, no periodicity was observed, the reduced iron gradually forming a permanent deposit. Experiments have also been conducted in hydrochloric acid in which the ferrous sulphate has been replaced by an equivalent quantity of nickel chloride or cobalt chloride. In the case of nickel chloride, reduction did not take place in acid solution, and in neutral solution the hydroxide was formed. Reduction of cobalt chloride in both hydrochloric and sulphuric acids readily took place, but a permanent deposit occurred without the advent of periodicity. In ammonium chloride solution, the phenomenon was more marked than in hydrochloric acid, but this system does not serve well from a quantitative point
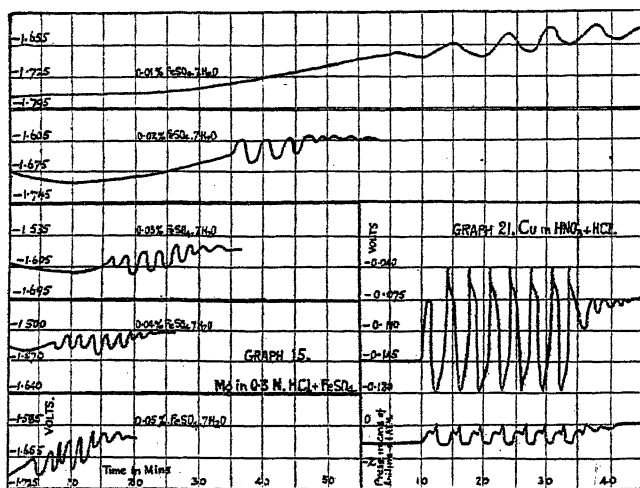
of view, since the solution quickly becomes alkaline with ammonia and reacts with the metal salt. Periodic phenomena similar to those described above have been observed with magnesium dissolving in 2% ammonium chloride solution with addition of 0·001% of crystallised cobalt chloride, 0·05% of crystallised ferrous sulphate, 0·001% of crystallised nickel chloride, or 0·002% of crystallised copper sulphate. The smallness of the quantities involved is characteristic of the conditions underlying periodic chemical action. In all these instances, the rate of evolution of hydrogen was also periodic. This may be a secondary effect, for it has been shown by the authors (this vol , p. 495) that couples of magnesium with these metals reduced in ammonium chloride solution are very active, decomposing water at the ordinary temperature. It is to be expected, therefore, that the rate of evolution of hydrogen would,

under these conditions, be dependent on the area of magnesium covered by the reduced metal.

Autoperiodic Systems.

With a view to obtain periodic phenomena from the simplest reacting systems, continuous measurements of the electro-potential of single activated metals reacting with a suitable solution have been made. The object has been to dispense with a separate second metallic component and incorporate it with the dissolving metal, causing the reacting electrode to function as its own activating agent.

Some experiments were carried out with aluminium, magnesium, and zinc after treatment by the usual methods. Aluminium, after vacuum-heat treatment or after scraping, in dissolving in hydrochloric acid registered a fluctuating potential, and a similar behaviour was noticed in the case of magnesium after vacuum-heat treatment. Magnesium gave a perfectly steady reading after scraping and attempts to activate zinc by either method were unsuccessful. The fluctuations were of the order of 0·02 volt and were rather rapid and very irregular, but the potential–time curve was very different from that obtained in the case of ordinary untreated aluminium or magnesium in hydrochloric acid. The changes were too small to affect the gas pressure.

The positive results served to demonstrate the possibility of constructing autoperiodic systems, though these particular cases did not lend themselves to quantitative development. The feeble activation which could be induced in these metals was very probably on account of the difficulty in hardening them and for this reason subsequent attention was devoted to copper, which has been found easily susceptible to activation. In all the experiments cited below, the copper was activated by cold rolling to the specified thickness from an original thickness of 0·022 in.

Activated copper, dissolving in nitric acid, showed no sign of periodicity, but continuous observation over the course of several hours of the potential of activated copper in hydrochloric acid revealed a slow oscillation—about one wave per hour. Copper slowly dissolves in hydrochloric acid containing atmospheric oxygen. By substituting nitric acid for the oxygen, attempts were made to increase the frequency.

Graph 21 was obtained from copper (rolled out to 0·0105 in.) dissolving in an acid mixture containing 25 c.c. of nitric acid (d 1·42), 10 c.c. of hydrochloric acid (d 1·16), and 65 c.c. of water. The graph illustrates the synchronous periodic variation in the potential of the copper electrode and in the pressure of the evolved

gas. The negative pressures recorded require some explanation : the gas evolved consists mainly of nitric oxide, which reacts with atmospheric oxygen with decrease in volume of the gaseous system as a whole. The fine capillary delays the entry of air and the pressure of gas in the apparatus is therefore slightly below atmospheric.

The series of changes to be observed at the surface of the dissolving metal under these conditions is most striking. Initially, the surface preserves its natural colour : then there is a sudden appearance of a black film deposited in the form of vertical streaks : the black film next turns dull grey : this is followed by a sudden flash due to the film turning white : the film then dissolves, leaving the metal with its original colour. Then the black film forms again, the whole cycle being repeated in each oscillation. After the point where the amplitude of the waves suddenly decreases (see Graph 21), the oscillation is between the black and the grey film, and the white film no longer appears; finally, the black film becomes permanent and the pulsations cease. This cessation is due not to any change in the metal but to a change in the composition of the solution during the progress of the reaction, for when the metal, in this final state, is removed from the solution and placed in a new acid mixture the oscillations recommence. The onset of the black film is marked by a movement of the electropotential in the positive direction and by an increase in the rate of evolution of gas, whilst, corresponding with the gradual turning grey of the film, the electropotential and the gas pressure slowly move towards their former values. The sudden appearance of the white film is accompanied by a rapid change of the electropotential in the negative direction and an equally rapid increase in the rate of gas production. The latter effect is easily visible, resembling a miniature eruption. As the white film dissolves, both the electropotential and the gas pressure regain their initial values.

The limits between which the concentration of the various components of the solution can be varied are narrow. Thus, the mixture 25 c.c. of nitric acid, 10 c.c. of hydrochloric acid, 65 c.c. of water always produced the periodic phenomena when acted on by rolled copper, but, if the total volume of solution was kept constant at 100 c.c. and the amount of hydrochloric acid at 10 c.c., mixtures containing 30 c.c., 20 c.c., or 27·5 c.c. of nitric acid did not favour the production of periodicity. Similarly, if the amount of nitric acid was kept constant at 25 c.c. and the total volume again at 100 c.c., mixtures made up with 15 c.c., 5 c.c., or 12·5 c.c. of hydrochloric acid did not give a periodic reaction. For this reason, in order to secure uniform conditions throughout the experi-

ments, a large stock of the standard acid mixture was made up and 100 c.c. were withdrawn for each experiment. Other more widely divergent mixtures were tried, but in these cases the reaction pursued a quite steady course. The concentration of the two acids being kept in the optimum ratio, 25 c.c. of nitric acid : 10 c.c. of hydrochloric acid, the best effect is produced by using 70 c.c. of water, thus making the total volume 105 c.c. No periodicity was observed when the amount of water used was 45 c.c. or 55 c.c. Using 75 c.c. of water, the electropotential and the gas evolution both became periodic, but the film forming over the copper surface alternated between the grey and white forms, the black film never appearing, and the frequency was higher than in the preceding experiments. Thus, under different conditions, the oscillation may be between the grey and white, grey and black, or black and white films : in the former two cases, the amplitude of the electrical effect is correspondingly smaller.

Some experiments have been performed with copper rolled to different thicknesses from the original 0·022 in. sheet. The unrolled copper was incapable of furnishing a periodic reaction under these conditions. Similarly, a piece which had suffered slight deformation by rolling to 0·020 in. was non-periodic. The other specimens, which were rolled to 0·010 in., 0·009 in., 0·0085 in., 0·007 in., and 0·004 in., respectively, all produced the periodic phenomenon and at approximately the same frequency. A sample of the 0·0085 in. copper, after keeping for 3 days, retained its inherent periodicity unabated.

Summary.

Some typical examples of periodic reactions which have been described previously by the authors have now been investigated from the electrochemical standpoint, using an apparatus in which the electrical and chemical effects of the reactions could be registered simultaneously. In the case of activated metallic couples dissolving in hydrochloric acid or ammonium chloride, the difference of potential between the couple as a whole and the solution, and between the two components of the couple undergo periodic fluctuations which synchronise with the periodic evolution of gas. A difference of potential exists between the activated and inactive forms of a metal. Some new reactions, involving the periodic deposition of metals, are described. The change consists in an alternate formation and dissolution of a metallic film which is accompanied by a corresponding oscillation of the electropotential. In some cases, the rate of evolution of hydrogen is also periodic. Examples are given of " autoperiodic " reactions, where one electrode serves both as the reacting metal and as the activating

N N 2

agent. The best case is furnished by copper, activated by cold rolling, dissolving in a mixture of nitric and hydrochloric acids : this example furnishes very regular waves representing both the electropotential and the pressure of the evolved gas. This is accompanied by a striking series of visible changes in a film formed over the metal surface. The effect of varying the concentration of acids has been studied and the optimum mixture consists of 25 c.c. of nitric acid (d 1·42), 10 c.c. of hydrochloric acid (d 1·16), and 70 c.c. of water.

The results of several previous experimenters are correlated with the authors' investigations on periodicity as a general principle.

CXL.—*The Photochemical Decomposition of Nitrosyl Chloride.*

By EDMUND JOHN BOWEN and JOHN FREDERICK SHARP.

THE photochemical decomposition of nitrosyl chloride has been studied by Kiss (*Rec. trav. chim.*, 1923, **42**, 665). Our experiments on the application of the photochemical equivalence law seem to throw light on the mechanism of the decomposition, and to offer an opportunity for a criticism of the interpretation placed by Kiss on his results.

Nitrosyl chloride was prepared in sealed all-glass apparatus by gently warming dry sodium chloride with nitrosylsulphonic acid and condensing the gas in a freezing mixture. The liquid was fractionated and the vapour allowed to fill a glass bulb connected to an all-glass manometer of the Jackson type (J., 1911, **99**, 1066), which had been thoroughly exhausted with two mercury vapour pumps backed by a Hyvac oil pump, the bulb being then sealed off from the vessel containing the liquid. An arm connected to the bulb contained phosphoric oxide, so that the gas, which had already passed over phosphoric oxide, was further dried *in situ.* The bulb was illuminated by the light from an automatically regulated carbon arc (10 amp.), passing through a condenser, a trough of dilute copper sulphate solution, and a gelatin colour filter. The reaction was followed by the change of pressure, the

glass manometer being sensitive to 0·15 mm. The amount of decomposition was measured at intervals up to 10 minutes, being then about 10%, experiment showing that the rate of the back reaction $2NO + Cl_2 \rightarrow 2NOCl$ over this range was negligible compared with the photochemical decomposition rate. The light absorption remained constant over this range, and the decomposition curve was linear, except for an initial acceleration lasting about 3 minutes, due to thermal expansion. This thermal expansion could not be eliminated by immersing the bulb in water, but could easily be eliminated graphically.

The energy in the light passing the filters, the absorption by the gas (about 90%), and the reflection losses (10%) from the glass surfaces were measured directly with a Moll thermopile connected to a millivoltmeter. This was calibrated by means of Leslie cubes containing boiling water and boiling aniline, allowance being made for the fact that lamp-black surfaces emit and absorb only 90% of black-body radiation, and the usual precautions being taken.

The following is a table of results, each value being a mean rate of change deduced from the linear part of the curve of a complete experiment. In order to produce a sufficiently rapid change to avoid the influence of the back reaction, filters allowing a large range of wave-lengths to pass were necessary. The number of quanta are calculated for a mean wave-length 4700 Å., i.e., $hv = 4\cdot2 \times 10^{-12}$ erg. Calibration of thermopile : 1 millivolt = $4\cdot45 \times 10^{-5}$ erg per second. Initial pressure of $NOCl = 456$ mm.

Spectral range of light. Å.	Pressure change per min. in mm.	Molecules decomposed per second.	Quanta absorbed per second.	Ratio : Quanta Molecules.	
5000—4380	3·3	$4\cdot11 \times 10^{17}$	$8\cdot34 \times 10^{17}$	2·03	Bulb in const. temp. bath.
,,	3·1	3·85 ,,	8·34 ,,	2·17	,, ,,
,,	3·8	4·74 ,,	10·1 ,,	2·13	
,,	4·3	5·28 ,,	10·1 ,,	1·91	
5200—4480	2·5	3·11 ,,	6·5 ,,	2·09	Bulb in const. temp. bath.
,,	3·0	3·74 ,,	7·9 ,,	2·11	

Two quanta appear to be absorbed for each molecule decomposed. This makes it likely that the process is a true unimolecular reaction, $NOCl + hv \rightarrow NO + Cl$, followed by spontaneous reactions re-forming nitrosyl chloride, such as the removal of chlorine atoms giving the transitory compound $NOCl_2$ suspected by Trautz and Hinck (Z. anorg. Chem., 1916, 97, 127) in measurements of the thermal combination of nitric oxide and chlorine.

The heat of formation of nitrosyl chloride is 18,000 cal. (Trautz

and Hinck), from which, taking the heat of dissociation of chlorine as 54,000 cal., we have :

$$NOCl + 45,000 \longrightarrow NO + Cl;$$
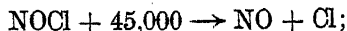
that is, the minimum wave-length capable of dissociating nitrosyl chloride is 6270 Å. This point is almost exactly where the absorption of nitrosyl chloride begins; the substance having weak bands from 6200 to 5300 Å., strong absorption beginning at 5250 Å. (Magnanini, *Z. physikal. Chem.*, 1889, 4, 427). Attempts to show that absorption by the red bands of nitrosyl chloride lead to dissociation were unsuccessful because of the small amount of light absorbed.

The above conclusion is not in accordance with Kiss's interpretation. Using white light, and carrying the decomposition further, he calculates constants from his results from a knowledge of the back reaction and assuming that the decomposition follows a unimolecular equation. On the present view, which is the only one compatible with the quantum mechanism of the process, the decomposition, though unimolecular in essence, will proceed at a rate determined by the amount of light absorbed. The light absorbed cannot have varied appreciably in Kiss's experiments, in which the maximum decomposition was about 10%; and in fact recalculation of his results assuming that the decomposition rate is constant, involving a 10% increase near the end of the reaction, greatly improves his constants.

One other conclusion of Kiss's must be criticised, namely, his very remarkable statement that the rate of combination of nitric oxide with chlorine is uninfluenced by light. If the photochemical change does take place and obeys the equivalence law, then the rate in his experiments should be

$$\text{Rate of decomp. of NOCl} \times \frac{Cl_2 \text{ absorption in white light}}{NOCl \text{ absorption in white light}}.$$

In Kiss's experiments, the first quantity is 0·3 mm. per minute, while the ratio of absorptions will be very small, say 1/20. Kiss's measured rate of thermal combination is 10 mm. per minute, from which it is clear that any photochemical change will be completely undetected when superimposed on the rapid thermal rate.

CXLI.—*The Mercuration of Aromatic Substances.*
Part I. Toluene.

By SAMUEL COFFEY.

LITTLE of the considerable amount of research that has been done on the mercuration of benzenoid compounds is of a quantitative character and some misconceptions of the positions taken up by the entering group appear to exist. Whitmore ("Organic Compounds of Mercury," 1921, p. 194) states that mercury apparently never enters the nucleus in the meta-position to an orienting group, but Holleman (private communication) has found that the mercuration product of nitrobenzene contains 40% and 50% of the *m*- and *o*-isomerides, respectively. The present investigation has been undertaken with the view of obtaining more quantitative information on these matters. Dimroth (*Ber.*, 1899, **32**, 761) has shown that toluene is easily mercurated and claims to have isolated *o*- and *p*-chloromercuritoluenes. Steinkopf (*Annalen*, 1917, **413**, 329), repeating the work, could not obtain pure products. The problem has now been more thoroughly investigated on quantitative lines.

Pure toluene was mercurated and after partial separation of the monomercuri- from the polymercuri-compounds the former were converted quantitatively into a mixture of bromotoluenes, which thermal examination showed to be a ternary mixture containing a considerable quantity of *m*-bromotoluene (compare van der Laan, *Rec. trav. chim.*, 1907, **26**, 29). The bromotoluenes were oxidised with dilute nitric acid to the bromobenzoic acids (compare Cohen and Miller, J., 1904, **85**, 174; Cohen and Dutt, J., 1914, **105**, 504), which were separated from one another by a method based on that described by Holleman (*Rec. trav. chim.*, 1915, **33**, 184).

A preliminary quantitative study of the oxidation by nitric acid of the three monobromotoluenes separately showed that the total bromotoluene could be accounted for and that the yields of the three acids were : *o*-, 87% ; *m*-, 90% ; *p*-, 92%.

By the method of separation used, which was extremely laborious, from 10 g. of the mixed acids there were obtained, in round figures, 4·5 g. of *p*-bromobenzoic acid and 1·3 g. of *m*-bromobenzoic acid. If, as is most likely, the remainder was the *o*-isomeride, and allowance be made for the different yields of bromobenzoic acids obtained by oxidation of the three bromotoluenes, the proportions of the three constituents of the mixture, and hence also of the three acetoxymercuritoluenes in the product of mercuration of toluene, are : *o* : *m* : *p* = 43 : 13 : 44.

This result is interesting, for in the bromination, nitration, and sulphonation of toluene the yield of m-compound is less than 5%. Taken in conjunction with Holleman's discovery mentioned above, it indicates that the course of mercuration is not dependent solely on the group already present.

EXPERIMENTAL.

Preparation of Pure Toluene.—The homogeneous mixture obtained by heating together pure p-toluenesulphonamide (100 g.), sulphuric acid (85 g.), and water (40 g.) at 200—210° was distilled with superheated steam at 200—220° until toluene ceased to pass over (3 hours). The oil was washed with sodium hydroxide solution, dried, and distilled (yield 45 g.; 83%). The toluene obtained on redistillation boiled within 0·1° at 109·4°/743 mm. and had a sweet aromatic odour quite unlike the sooty smell usually associated with this compound.

Mercuration of Toluene and Partial Separation of the Products.— Toluene was heated under reflux with mercuric acetate ($\frac{1}{5}$ part) for 5 or 6 hours. After 12 hours, the liquid was decanted, the insoluble polymercurated toluene washed with toluene and a little acetic acid, and the solution and washings were distilled until the temperature was 120°. The residue was poured into a solution of potassium bromide, the remaining toluene distilled as rapidly as possible in steam, and the bromomercuritoluenes were collected, washed, and dried. Attempts to determine the mercury in this mixture by the usual rapid methods were unsuccessful. The amount of polymercurated toluene obtained (as chlorides) from the insoluble product of the reaction was less than one-tenth of the yield of crude bromomercuri-compounds. All the mercuric acetate was accounted for as mercurated toluene.

Conversion of the Bromomercuritoluenes into Bromotoluenes.—The bromomercuritoluenes, suspended in well-cooled chloroform, reacted almost instantly with bromine (1 equiv.), added slowly. After filtration, the mercuric bromide was washed with chloroform, the solvent removed from the filtrate and washings on the water-bath, and the bromotoluenes were distilled in steam and fractionally distilled three times, the fractions finally obtained from 74 g. of the crude bromomercuri-compounds being : 181—190°, 25 g. (temperature rose very rapidly from 186° to 190°); 190—210°, 2 g.; 210—250°, 2·5 g.; and above 250°, 1 g.

The main fraction consisted of pure monobromotoluenes and the remainder of dibromotoluenes (b.p. 230—245°), but there was no substitution in the side chain. The crude monobromomercuritoluenes prepared in this way are therefore considerably con-

taminated with polymercurated compounds (roughly 15%). About 95% of the bromomercuri-compounds were accounted for. The main fraction of monobromotoluenes showed a well-defined freezing point at —10·8°, a second less marked one at —53°, and was still partly liquid at —78°. Hence it was a mixture of all three iso-merides, not a simple mixture of ortho- and para-isomerides, which gives a eutectic at —38°.

Oxidation of the Monobromotoluenes.—The pure bromotoluenes were prepared from specially purified amines by van der Laan's method (*loc. cit.*). The *p*-bromotoluene melted at 26·4° instead of 26·7° and the *o*-compound at —27° instead of —26°.

The bromotoluene (2 g.) was heated with 10 g. of dilute nitric acid ($1HNO_3 : 3H_2O$) at 130° for 8 hours (Cohen and Miller, *loc. cit.*). The product was neutralised with caustic potash, the small amount of insoluble oil (mainly, if not wholly, bromonitrotoluenes) removed with ether, and the acids were precipitated with nitric acid and dried in a vacuum; a further small quantity was extracted from the aqueous solution with ether. The small amount of hydrogen bromide in the aqueous solution, determined by titration with silver nitrate, was a measure of the bromotoluene which had been completely oxidised.

The results given in the table are the means obtained from several concordant determinations.

Bromotoluene.	% insol. in ether.	% as free HBr.	% as acid.
Ortho	5·4	10·0	87·2
Meta	4·4	2·3	90·0
Para	1·4	3·9	92·4
Mixed	3·4	6·6	91·2

Separation of the Bromobenzoic Acids.—Preliminary experiments showed that boiling saturated aqueous solutions contain about 4%, 1·0%, and 0·15% of the *o*-, *m*-, and *p*-acid respectively, and that the solubilities of the barium salts are : at 18°, *o*-, 23% ; *m*-, 0·65% ; *p*-, 0·85% : at 100°, *m*-, 3·4 g., and *p*-, 2·25 g., per 100 c.c. ; yet the *p*-salt is described in the literature as readily soluble.

The mixture of acids obtained above (10 g.) was extracted thrice with 200 c.c. of boiling water for 3 hours. The residue (3·70 g.), m. p. 256°, was pure *p*-bromobenzoic acid (the m. p. of which is usually given as 251°).

The aqueous extracts were neutralised with baryta, gradually evaporated and allowed periodically to crystallise. Mixtures of barium salts separated in characteristic nodules until the volume of the solution was 30—40 c.c., when the readily soluble ortho-salt began to crystallise. The mixture of barium salts was crystallised

from water six or more times, when the pure *m*-salt was obtained. (A mixture of barium *m*-bromobenzoate with a small quantity of the *p*-isomeride behaved similarly.) The sparingly soluble barium salts were dissolved in water and fractionally precipitated with *N*/10-hydrochloric acid, first, impure *p*-acid and then impure *m*-acid being obtained. Finally, 0·6 g. of pure *p*-bromobenzoic acid was isolated, making 4·3 g. altogether. The impure *m*-acid was again converted into the barium salt, the latter systematically crystallised to free it from the readily soluble *o*-salt, and then reconverted into the acid, which was recrystallised once from water. Altogether 1·20 g. of acid melting at 145—149° were obtained; a mixture of *m*-bromobenzoic acid and 10% of the *p*-isomeride also melted at this temperature, and a mixed melting point gave 145—149°. By continued fractionation of the barium salts pure *m*-bromobenzoic acid was obtained. Thus 4·42 g. of *p*-bromobenzoic acid and 1·08 g. of the *m*-isomeride were isolated from 10 g. of the mixed acids. The mother-liquors (45 c.c.) containing the *o*-salt probably contained barium salt equivalent to 0·2 g. of the *m*-acid. The total quantity of *m*-bromobenzoic acid present in 10 g. of the mixed acids was therefore about 1·3 g.

The mother-liquors containing the very soluble barium salts gave on acidification a good yield of impure *o*-bromobenzoic acid.

CXLII.—*A Synthesis of* 1 : 2-*Dihydroquinaldine.*

By FREDERICK ALFRED MASON.

1 : 2-DIHYDROQUINALDINE, which was prepared by Räth by heating together *o*-toluidine and α-chloropropaldehyde diethylacetal (*Ber.*, 1924, **57**, 555), has now been synthesised by a method * employing cheap and readily obtainable materials. Aniline condenses with β-chlorobutaldehyde diethylacetal, under the conditions stated later, to give β-*anilinobutaldehyde diethylacetal,* which is

* The investigation was begun in 1923 before the publication of Räth's results, but had to be suspended for some time and was completed in 1924.

converted into 1 : 2-dihydroquinaldine by treatment with phosphoric anhydride in benzene solution :

$$CHMeCl\cdot CH_2\cdot CH(OEt)_2 \xrightarrow{NH_2Ph} NHPh\cdot CHMe\cdot CH_2\cdot CH(OEt)_2 \xrightarrow{-2EtOH}$$

$$C_6H_4 \Big\langle \begin{matrix} CH{=}CH \\ NH\cdot CHMe \end{matrix}$$
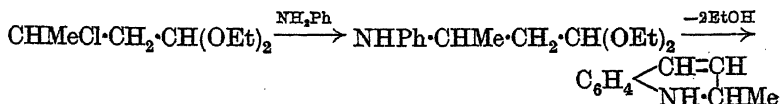
Attempts to close the ring by means of strong or dilute hydrochloric acid, glacial acetic acid or acetic anhydride gave negative results.

β-p-*Ethoxyanilinobutaldehyde diethylacetal*,

$$CHMe(NH\cdot C_6H_4\cdot OEt)\cdot CH_2\cdot CH(OEt)_2,$$

obtained by using p-phenetidine in place of aniline, on treatment with phosphoric anhydride in benzene solution, gave a small amount of an oil, b. p. 260—270°, which did not appear to be the expected p-ethoxydihydroquinaldine.

Aniline and crotonaldehyde diethylacetal were heated together in alcoholic solution, but β-anilinobutaldehyde diethylacetal could not be detected in the product. Attempts to condense aniline with β-chlorobutaldehyde diethylacetal by means of sodium amyloxide also failed, the product consisting, probably, of a mixture of aniline and crotonaldehyde diethylacetal, so that here also there was no evidence that aniline could add on to the nascent double bond. This is of interest as indicating that in the Doebner-Miller quinaldine synthesis the reaction probably takes place according to equation (1) rather than (2) (compare Blaise and Maire, *Bull. Soc. chim.*, 1907, **3**, 667) :

$$CHMe{:}NPh + H\cdot CH_2\cdot CH{:}NPh = CHMe(NHPh)\cdot CH_2\cdot CH{:}NPh \quad (1)$$
$$CHMe{:}CH\cdot CHO + 2NH_2Ph = CHMe(NHPh)\cdot CH_2\cdot CH{:}NPh + H_2O \quad (2)$$
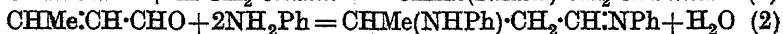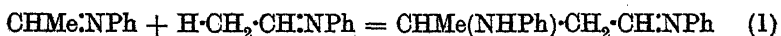
Neither quinaldine nor dihydroquinaldine was recognised in the product obtained on heating together aniline and β-chlorobutaldehyde diethylacetal in the way used by Räth for his synthesis.

EXPERIMENTAL.

β-Chlorobutaldehyde diethylacetal was prepared from crotonaldehyde and absolute alcohol saturated in the cold with hydrogen chloride, by Wohl and Frank's method (*Ber.*, 1902, **35**, 1904). The yield was only about 50% (Wohl claimed 66%), but no improvement was effected by the addition of calcium chloride or otherwise varying the conditions.

β-*Anilinobutaldehyde Diethylacetal.*—A mixture of freshly-distilled β-chlorobutaldehyde diethylacetal (25 c.c.), dry amyl alcohol (50 c.c.), powdered, well-dried potassium carbonate (25 g.), copper

powder (1 g.), and sodium iodide (2 g.) was shaken and kept for
5 minutes and, after addition of redistilled aniline (13 c.c.), heated
under reflux for 48 hours. The cooled liquid was filtered, the
residue washed with a little amyl alcohol, and the combined filtrates
were distilled until the amyl alcohol was removed; the distillation
was then continued at 25 mm. and gave the following fractions :
100—150°, 25 c.c. ; 150—170°, 18 c.c. ; 170—190°, 3 c.c. After
refractionation, 18 c.c. of a clear yellow, slightly viscous oil were
obtained, b. p. 173—175°/25 mm. or 153—154°/12 mm. Yield
17·9 g. or 56% (Found : C, 70·8;, H, 9·7; N, 5·9. $C_{14}H_{23}O_2N$
requires C, 70·9; H, 9·7; N, 5·9%).

The substance gave, in ethereal solution, a yellow *picrate* crystal-
lising from alcohol in yellow spangles, m. p. 188—190°, and in
dilute hydrochloric acid a yellow precipitate with platinic chloride
which quickly became tarry.

In one experiment, the copper powder was omitted, but the
yield remained about the same; in other cases again, although the
experimental conditions were apparently the same, the yield was
practically negligible, the product consisting of viscous, high-boiling
gums.

β-p-*Ethoxyanilinobutaldehyde diethylacetal* was prepared in a
similar manner to the anilino-compound, using β-chlorobutaldehyde
diethylacetal (55 c.c.), amyl alcohol (75 c.c.), potassium carbonate
(50 g.), sodium iodide (4 g.), and p-phenetidine (41 g.), but no
copper powder. The mixture having been heated under reflux for
28 hours, and the product fractionated, 56 g. of the acetal were
obtained, b. p. 190—192°/12 mm. (yield 68%). It formed a pale
yellow, slightly viscous oil which was slightly heavier than water
(Found : C, 68·3; H, 9·7. $C_{16}H_{27}O_3N$ requires C, 68·3; H, 9·6%).
With an ethereal solution of picric acid, it gave an orange-yellow
coloration, but no picrate separated.

An attempt to prepare the p-chloroanilino-compound gave no
definite product except a very small amount of a substance which,
after recrystallisation from alcohol, melted at 95—97°.

1 : 2-*Dihydroquinaldine.*—β-Anilinobutaldehyde diethylacetal (10
c.c.) was dissolved in well-dried benzene (50 c.c.) and phosphoric
oxide (10 g.) was added by degrees. After standing over-night at
room temperature, the mixture was heated under reflux for 6
hours and cooled, and ice and water were added until practically
all was in solution. The aqueous layer was washed with benzene,
made alkaline with ammonia, the oil extracted twice with ether
and dried over potassium carbonate. The product on fractionation
at 20—25 mm. gave 3 c.c., b. p. 130—160°, which after refraction-
ation gave 2·2 c.c. of a pale yellow liquid, b. p. 125—130°/18 mm.

(Found : C, 82·7; H, 7·6; N, 9·7. Calc., C, 82·8; H, 7·6; N, 9·6%). It had an odour resembling that of quinaldine, decolorised permanganate, and agreed generally with Räth's description of the substance.

The oil darkened on keeping in a sealed tube and formed a picrate melting at 192—193°, after recrystallisation from alcohol.

An attempt was made to close the ring of *p*-ethoxyanilino-butaldehyde diethylacetal (10 c.c.) in a similar manner. About 2 c.c. of an oil were obtained, b. p. 260—270°/760 mm. It formed a picrate, m. p. 190°.

Treatment of the oil with a few drops of cold concentrated hydrochloric acid gave a crystalline hydrochloride, m. p. 234—236° (decomp.), after recrystallisation from a very little methyl alcohol, in which it was extremely soluble. The chlorine found (20·6%) did not correspond to any simple expected derivative (*p*-ethoxydihydroquinaldine hydrochloride contains only 15·7% Cl). The quantity obtained did not suffice for a complete analysis.

Attempt to Condense Aniline and Crotonaldehyde Diethylacetal.— On heating together under reflux the acetal (prepared in 80—90% yield by Frank and Wohl's method) and aniline for 6 hours and distilling the product, neither dihydroquinaldine nor anilinobut-aldehyde diethylacetal was found, nor on heating the distillate with sodamide was either of these products detected.

On heating together aniline (28 c.c.) and β-chlorobutaldehyde diethylacetal (25 c.c.) in a sealed tube at 220° for 5 hours (compare Räth's method), a dark brown oil was formed which, on being worked up, gave the following fractions at 20 mm. : 90—110°, 8·5 c.c.; 110—150°, 9 c.c.; 150—165°, 3 c.c.; together with a large amount of tar. The middle fraction afforded a picrate which melted at 170° and was therefore not dihydroquinaldine.

A mixture of aniline and β-chlorobutaldehyde diethylacetal, left in a sealed tube at room temperature for 5 months, became pasty with fine needles of aniline hydrochloride; as all the residue, however, distilled below 100°/40 mm., very little condensation can have been effected and the aniline probably merely removed hydrogen chloride to give crotonaldehyde diethylacetal.

CXLIII.—*The Hydrates of Calcium Carbonate.*

By JOHN HUME.

IN " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," where there is given (1923 ed., vol. iii, p. 824) a list of references to investigations of the hydrated forms of calcium carbonate carried out since 1819, Mellor sums up the evidence for the existence of various hydrates in the following sentence : " With indecisive evidence of this nature, it appears as if there is a di- or tri-hydrocalcite, and a penta- or hexa-hydrocalcite, or, possibly, mixtures of colloidal calcium carbonate with the anhydrous salt." Copisarow (J., 1923, **123**, 785) describes the preparation of crystals of calcium carbonate pentahydrate and states that no crystalline modification having the composition $CaCO_3,6H_2O$ recorded by Pelouze (*Compt. rend.*, 1865, **60**, 429) could be detected. Mackenzie (*ibid.*, 2409) has shown that $CaCO_3,6H_2O$ can be prepared in 10% sugar solution between 0° and 10°, but he was unable to determine the temperature of transition from the hydrated to the anhydrous state.

In the present work, begun with the object of ascertaining what hydrates actually exist and the conditions necessary for their existence, the crystals were prepared in, and kept in contact with, a 20% aqueous solution of sucrose. In this solution, a hexahydrate exists below 10·4°, and a pentahydrate below 17·0°. The hexahydrate in contact with water at or above 0° changes slowly into anhydrous calcium carbonate (compare Johnstone, Merwin, and Williamson, *Amer. J. Sci.*, 1916, **41**, 471). The same is probably true of the pentahydrate. All dilatometer experiments have shown a break at 25° in the volume–temperature curve, and this suggests that a hydrate lower than the pentahydrate may exist, but, so far, all attempts to obtain confirmation have failed. Under the experimental conditions, the temperatures of transition were quite definite, but possibly they would be altered by varying the concentration of the sugar solution. It is also possible that the hydrates may be metastable even in contact with sugar solution, and may decompose exceedingly slowly.

The formation of crystals of the hexahydrate from sugar-lime solutions at temperatures up to 17° (Mackenzie, *loc. cit.*) has been confirmed. It is explained by the fact that between 10·4° and 25·0° the metastable hexahydrate is first precipitated, and changes slowly into the form stable at the temperature of the experiment.

EXPERIMENTAL.

The hexahydrate crystals were, as a rule, prepared as follows : A solution of sucrose (25 g.) in water (100 c.c.) was shaken with

calcium oxide (freshly prepared from precipitated calcium carbonate) and filtered as quickly as possible to prevent absorption of much carbon dioxide. Carbon dioxide was bubbled through the filtrate at 0° for 5—10 minutes, no precipitate forming, and the solution was then exposed at 0° to the action of atmospheric carbon dioxide. After 2 or 3 days, well-defined crystals separated, which could be preserved in sugar solution for a considerable period (possibly indefinitely) if the temperature were kept down; crystals kept thus for 7 weeks showed no loss of water on analysis. In other experiments, the sugar concentrations were 50 g., 30 g., and 20 g. in 100 c.c. of water, and in each case crystals of the hexahydrate were obtained at 0°. Mackenzie (*loc. cit.*) obtained the same product from more dilute solutions.

The largest crystals were best obtained by omitting the passage of carbon dioxide and allowing the lime-sugar solution to absorb carbon dioxide very slowly from an atmosphere poorer in carbon dioxide than the laboratory air.

Many preparations were made and the crystals were washed with iced water, with absolute alcohol, and with ether, thrice in each case (Found : loss at 100°, 50·3, 49·9, 50·4, 51·6, 50·8, 49·6, 52·7, 49·4, 51·4, 50·3. Calc. for $CaCO_3,6H_2O$: H_2O, 51·9; for $CaCO_3,5H_2O$: H_2O, 47·4%).

In two analyses, the following results were obtained by heating the crystals in a stream of oxygen and absorbing the water in a calcium chloride tube, the carbon dioxide in a soda-lime tube, and weighing the residue of calcium oxide (Found : CaO, 27·45, 27·3; CO_2, 21·5, 22·3; H_2O, 51·5, 50·3. Calc. for $CaCO_3,6H_2O$: CaO, 26·9; CO_2, 21·1; H_2O, 51·9%).

The density of the crystals, $d^{15°}$ 1·789, was determined by the floating method in methylene iodide–benzene (compare Mackenzie, *loc. cit.*).

To investigate the stability of the hexahydrate in contact with water, crystals of known water-content were kept in water at 0° and samples were withdrawn from time to time and analysed [Percentage of water found : (i) initial, 49·6; after 7 days, 5·6 (ii) initial, 52·7; after 8 days, 5·3. (iii) initial, 49·4; after 2 days 39·8; after 4 days, 14·7].

The results showed that it was useless to carry out dilatometric experiments with the crystals in contact with water. Accordingly to determine whether the hexahydrate changed into lower hydrates at temperatures above 0°, the crystals and their mother-liquor were placed in a dilatometer, specially designed for easy filling at temperatures below atmospheric (Hume, *Chem. News*, 6th June 1924). The temperature had to be raised exceedingly slowly, and

it was necessary to design a modified thermo-regulator for the purpose (Hume, *J. Soc. Chem. Ind.*, 1924, **43**, 250). Many temperature and volume readings were taken, and the curves plotted from the data of three experiments are reproduced. A blank experiment was done with sugar solution of the same concentration as was used in the preparation of the crystals, and this gave a normal expansion curve.
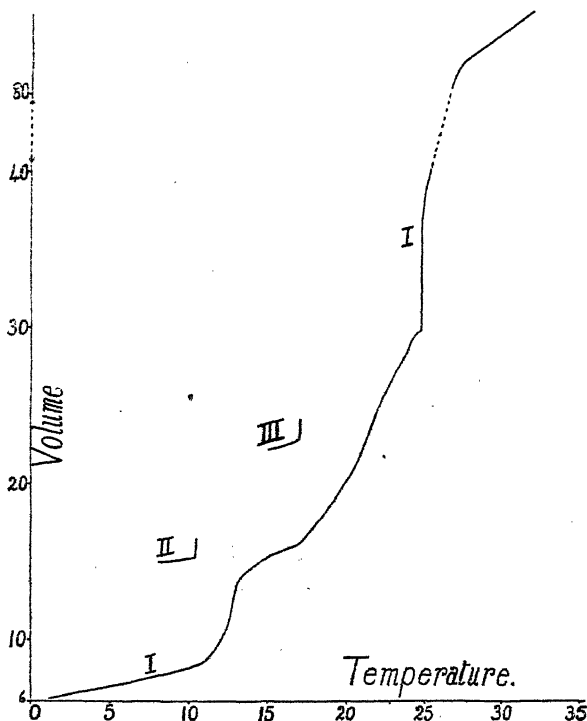
Curve I (crystals prepared at 0°) shows a transition beginning at about 11·3°, and another at about 17·3°. The latter involved a large volume change, and before it was quite complete the temperature reached 25°. Here an even larger increase of volume was observed. After expansion ceased, the crystals contained 0·7% of water.

Curve II (crystals prepared at 0°) shows the results of an experiment in which the temperature was raised at the rate of 0·1° per day. The first break in the curve is at 10·4°. When constant volume was reached at this temperature, the crystals contained 47·5% of water. A density determination by floating the crystals

in methylene iodide and benzene at 15° gave the value 1·835. The crystals from a duplicate experiment had a water-content of 47·0% and a density of 1·833.

Crystals prepared by the method described above for the hexa-hydrate, but at 11·6°, contained 47·2% of water and had $d^{15°}$ 1·830 and 1·833. A sample of these crystals was used for a dilatometer experiment; the results, given in Curve III, show a transition beginning at about 17°.

All attempts to prepare a definite hydrate from sugar-lime solutions kept at 18° were unsuccessful. Fresh hexahydrate crystals were therefore introduced into two dilatometers, kept at 24°. Expansion took place for 4½ months, and when it ceased, the crystals were anhydrous, and of density 2·6. No confirmation, therefore, of the existence of a trihydrate, or of any hydrate lower than a pentahydrate, was obtained, although such may exist between 17° and 24°. Also the break in the curves at 25° has, so far, not been accounted for.

The crystals obtained when calcium carbonate was precipitated at 0° in glycerol solution and in 10% sodium hydroxide solution contained 51·5% and 51·5% of water respectively.

Attempts were made to determine the vapour pressure of the hexahydrate by keeping crystals of it in an evacuated bulb attached to a manometer. The pressure in the bulb increased to that of saturated water vapour, and thereafter remained constant, while the dehydration of the crystals proceeded to completion. It is therefore concluded that the vapour pressure, or rather the decom-position pressure, of the hexahydrate is above the vapour pressure of water at temperatures above 0°.

Further attempts are being made to isolate a hydrate lower than the pentahydrate, and experiments are in progress to deter-mine the decomposition pressures of the hydrates.

CXLIV.—*The Interaction of Thiocyanogen with Unsaturated Compounds.*

By FREDERICK CHALLENGER and THOMAS HAROLD BOTT.

THE product obtained from thiocyanogen and styryl methyl ketone (J., 1923, **123**, 1055) is a monothiocyano-substitution derivative, CHPh:C(SCN)·COMe(I). The molecular weight in benzene corre-sponds with this formula and not with [COMe·CH(SCN)·CHPh]₂ (II), whilst the structure SCN·CHPh·CH(SCN)·COMe (III) is

excluded by analysis.   Other evidence in this direction is furnished by reduction, oxidation, and the action of bromine (see experimental section).   The thiocyano-group is not in the nucleus, whilst the structure CHPh:CH·CO·CH$_2$·SCN is improbable.   Moreover, distyryl ketone and thiocyanogen give a compound analogous to (I) containing two thiocyano-groups.   Here a methyl radical is absent.

From the results described previously (loc. cit.), and the work of Kaufmann and Liepe (see J., 1924, 125, 1377) on the interaction of thiocyanogen with ethylene, amylene, and antipyrine, it is probable that styryl methyl ketone first gives (III), which then loses thiocyanic acid.   By analogy with similar reactions, a compound of structure (I) should result.   This is in agreement with the work of Dufraisse (Compt. rend., 1920, 171, 1062; 1921, 173, 985) and of Pauly and Berg (Ber., 1901, 34, 2093) on ethylideneacetone dibromide.

The bromostyryl methyl ketone of Ruhemann and Watson (J., 1904, 85, 456) was assumed by these authors to have the β-structure CPhBr:CH·COMe by analogy with the bromostyryl phenyl ketone which Wislicenus (Annalen, 1899, 308, 219) regarded as CPhBr:CH·COPh.   This has now been shown by Dufraisse (loc. cit.) to have the α-structure CPhH:CBr·COPh.   Hence it is probable that the product of Ruhemann and Watson also is an α-derivative.

The compound obtained from carvone and thiocyanogen contains only one thiocyano-group.   Owing to the very poor yield obtained and the inability of one of us to continue the investigation, the substance has not been further examined.   On the assumption that the double bond in the side chain is unattacked the most probable constitution would appear to be

$$CH_2\text{:}CMe\text{·}CH < ^{CH=CH}_{CH_2\text{·}CO} > C(SCN)\text{·}CH_3,$$
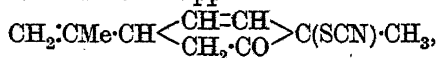
but others are clearly possible.

When styryl methyl ketone dibromide is boiled with alcoholic potassium thiocyanate, the ketone is regenerated, and polymerised thiocyanogen obtained.   Wheeler and Merriam (J. Amer. Chem. Soc., 1902, 24, 441) obtained a similar result with dinitrostilbene dibromide.

EXPERIMENTAL.

α-Thiocyanostyryl Methyl Ketone (I).—Solutions in dry ether of styryl methyl ketone (10 g. [1/15 mol.] in 50 c.c.) and thiocyanogen (Soderbäck, Annalen, 1919, 419, 217) (1/15 mol. in 270 c.c.) were mixed and kept in the dark.   After 4 days the ethereal suspension of polymerised thiocyanogen was decanted from the crystalline

product. On fractionation from acetone–ligroin in presence of animal charcoal, 2·5 g. of white, glistening plates were obtained, m. p. 119° (Found: C, 65·2; H, 4·4; N, 7·0; S, 15·85; M, cryoscopic in benzene, 185. $C_{11}H_9ONS$ requires C, 65·0; H, 4·4; N, 6·9; S, 15·7%; M, 203).

Some unchanged ketone was obtained from the ethereal filtrate, but no other pure product could be isolated.

Thiocyanostyryl methyl ketone is also obtained, but in no better yield, by adding, during 2 hours, 10 g. of iodine in 50 c.c. of ether to 5 g. of styryl methyl ketone, 12·5 g. of mercuric thiocyanate, and 50 c.c. of ether.

Action of bromine. The thiocyano-ketone (2·04 g.) in 30 c.c of carbon disulphide was treated with 1·6 g. of bromine (1 mol.) in 10 c.c. of the same solvent. Decoloration was complete in some hours, but no hydrogen bromide was formed. After four crystallisations from alcohol, the *dibromide* formed long, white needles, m. p. 138° (decomp.) (Found : N, 4·0; Br, 43·25. $C_{11}H_9ONBr_2S$ requires N, 3·85; Br, 44·05%).

Oxidation. (*a*) Aqueous 4% potassium permanganate (100 c.c.) was boiled with 0·4 g. of the ketone for 4 hours, and excess of the reagent removed with hydrogen peroxide. Potassium sulphate, benzoic acid (m. p. 121°), and traces of a fatty acid were produced, but no diphenylsuccinic acid.

(*b*) The ketone (0·5 g.) was shaken for 6 hours with a solution of 1 c.c. of bromine and 4 g. of potassium hydroxide in 80 c.c. of water, and the mixture was extracted with ether and treated with sulphur dioxide. Cinnamic acid (m. p. and mixed m. p. 133°) was deposited.

Reduction. The ketone (1·5 g.) was boiled for 4 hours with 5 g. of zinc dust and 50 c.c. of water, and the mixture, which contained thiocyanate ions, was distilled in steam, giving benzylacetone (m. p. and mixed m. p. of semicarbazone, 131°). The residue, on extraction with alcohol, yielded traces of a solid, m. p. 157°. δε-Diphenyl-βη-octadione melts at 161°.

Distyryl Ketone and Excess of Thiocyanogen.—After 4 days, an ethereal solution of the reactants deposited a solid which, on crystallisation from acetone–ligroin, melted at 151° and gave a deep blue coloration with sulphuric acid (Found : N, 8·2; S, 18·4. $C_{19}H_{12}ON_2S_2$ requires N, 8·05; S, 18·4%).

Carvone and Thiocyanogen.—Carvone (10 g.) was added to a solution of thiocyanogen (see p. 1040). After 4 weeks the solvent was removed, and the oil washed with ligroin and extracted with acetone–ligroin. The concentrated extract was diluted with alcohol, and the white needles (1 g.) deposited after 4 days were crystallised

from alcohol; m. p. 254° (Found : N, 7·0; S, 15·7. $C_{11}H_{13}ONS$ requires N, 6·8; S, 15·5%).

CXLV.—*The Potassium Chlororutheniates and the Co-ordination Number of Ruthenium.*

By S. H. CLIFFORD BRIGGS.

By the action of alkali chlorides upon solutions of ruthenium trichloride, Howe (*J. Amer. Chem. Soc.*, 1901, **23**, 775) obtained compounds of the formula $M^I_2RuCl_5,H_2O$ analogous to the salt K_2RuCl_5,H_2O described by Miolati and Tagiuri (*Gazzetta*, 1900, **30**, 511), and named Miolati's series in the present paper. They give yellowish-brown solutions which are pure yellow when dilute and are not affected by chlorine or bromine vapour. Howe prepared a second series of compounds which are generally regarded as aquopentachlororutheniates with the molecule of water in the complex as shown by the formula $M^I_2(RuCl_5H_2O)$. These compounds are more soluble than the salts of Miolati's series and give solutions which are pink when very dilute and give an intense black coloration with chlorine or bromine. These compounds will be referred to below as Howe's series.

Since the water in Miolati's salt K_2RuCl_5,H_2O is very firmly attached and not completely given off at 200° (compare Gutbier, Falco, and Vogt, *Z. anorg. Chem.*, 1921, **115**, 230), the water molecule would appear to be a constituent of the complex in both series. As, however, the simple compound $K_2(RuCl_5H_2O)$ cannot exist in two isomeric forms according to the co-ordination theory (compare Briggs, *J.*, 1921, **119**, 1876), it was decided to make a further investigation of the potassium chlororutheniates.

It has been found that in Miolati's series there are at least two compounds having the formulæ K_2RuCl_5,H_2O and $2K_2RuCl_5,3H_2O$ respectively. In Howe's series, the only salt prepared in the pure state had the formula $2K_2RuCl_5,3H_2O$, although some slight evidence was obtained for the existence of other compounds having the formulæ K_2RuCl_5,H_2O and $K_2RuCl_5,2H_2O$.

The compound K_2RuCl_6 obtained by Howe (*J. Amer. Chem. Soc.*, 1904, **26**, 546) from the black solution produced by oxidising Howe's salt $K_2(RuCl_5H_2O)$ with chlorine, was not prepared during the

work now described, but a substance was obtained of which the analysis corresponded closely with the formula $K_2(RuCl_5OH, H_2O)$. As the details given in Howe's papers are very incomplete, it does not follow that the compound K_2RuCl_6 cannot be prepared.

A salt of the formula K_2RuCl_5, K_2RuCl_5OH was produced by the action of a current of air on a warm, acidified solution of the compound $2K_2RuCl_5, 3H_2O$ (Howe's series). It would therefore appear that in oxidation by chlorine or oxygen a hydrogen atom is removed from a co-ordinated water molecule, giving a hydroxo-compound.

The Co-ordination Number of Ruthenium in the Chlororutheniates.

It is evident that the co-ordination number of ruthenium is greater than 6 in the compounds $2K_2RuCl_5, 3H_2O$, and hexachloro-rutheniates with constitutional water have recently been prepared by Krauss (Z. anorg. Chem., 1921, **117**, 111) and by Aoyama (ibid., 1924, **138**, 249) having the formulæ Cs_2RuCl_6, H_2O and $2(NH_4)_2RuCl_6, H_2O$, respectively, in which the co-ordination number of ruthenium is also greater than 6.

If water molecules or chlorine ions are shared by the ruthenium atoms it is possible to write the compound $2K_2RuCl_5, 3H_2O$ in isomeric forms with co-ordination number 7 (one chlorine atom or water molecule shared) or with co-ordination number 8 (three bridging units shared). It does not appear probable that simple chemical methods will be found for determining the exact nature of these compounds, but an X-ray examination of the crystals might help to elucidate the problem, and such an examination is very much to be desired. Since there are exceedingly few co-ordination compounds with co-ordination number 7, in the author's opinion it is likely that the ruthenium atoms function with co-ordination number 8 in the compounds under review, and it should be noted that all the compounds described below might be formulated with this co-ordination number.*

* Attention has been directed to the fact that the co-ordination number 7 is in accordance with the electronic structure of ruthenium. If, however, tervalent ruthenium had the co-ordination number 7 as a result of the completion of the electron sub-groups as required by Sidgwick's theory (J., 1923, **123**, 725), then surely tervalent iron should also give compounds with co-ordination number 7. Now a very large number of complex compounds of tervalent iron have been prepared, but so far as I am aware in all these cases the co-ordination number is 6. If, in the extensive literature, there are to be found any examples with co-ordination number 7, they are certainly an extremely small proportion of the total.

My own view is that there are at least two factors involved in the determination of co-ordination number. One of these is the tendency to form spatially symmetrical compounds due to the fact that the affinity of the

EXPERIMENTAL.

The ruthenium trichloride was purchased from Messrs. Johnson, Matthey and Co. and was free from other platinum metals with the exception of a trace of rhodium. It was used without further purification in the earlier part of the investigation. The material was then worked up and purified by conversion into the tetroxide as described by Howe. The trichloride prepared from the tetroxide gave substances identical with the preparations from the unpurified trichloride.

For analysis, the compounds, after being dried in a vacuum over sulphuric acid, were reduced in a current of pure hydrogen, the evolved gases being led through a delivery tube which just dipped into a solution of silver nitrate slightly acidified with nitric acid and contained in a small wide-mouthed flask. The gases then passed through absorption bulbs containing a further quantity of the silver nitrate solution, which remained clear when the reduction was carefully performed. For accurate results, it was found necessary, after lixiviating the ruthenium residue, to repeat the reduction and lixiviation once or twice.

In some cases, water was estimated directly by combustion over lead chromate as in the analysis of organic compounds containing halogens. It was essential to do the combustion in oxygen. When air was used the results were too low.

Miolati's Series.—The salts of Miolati's series are formed when potassium chloride is added to a cold acidified solution of ruthenium trichloride. The precipitated compound is usually not homogeneous, but by recrystallisation from warm acidified water the compound K_2RuCl_5,H_2O was obtained by Gutbier, Falco, and Vogt

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central atom emanates from the nucleus and is directed equally towards all points on the surface of the atomic sphere. Co-ordination numbers 4, 6, and 8 are therefore common, corresponding to the corners of regular polyhedra circumscribed about the surface of the atomic sphere, in accordance with Werner's theory. We may describe this first factor as the *Werner* factor. The second factor, which may be termed the *Sidgwick* factor, is the tendency to form complete sub-groups of electrons as shown by Sidgwick (*loc. cit.*). When the two factors both tend to give the same co-ordination number, very stable and well-defined co-ordination compounds are produced; and it is to such compounds that Sidgwick directs special attention in his paper. In those cases in which the two factors tend to give different co-ordination numbers the Werner factor appears to exert the preponderating influence, and consequently there are very few compounds with co-ordination number 5 or 7. I therefore think it is much more probable that in the compounds described in this paper it will ultimately be found that ruthenium has the co-ordination number 8 rather than 7. Of course there is also the possibility that the series of Howe and Miolati represent compounds with different co-ordination numbers, 7 in one of the series and 8 in the other.—S. H. C. B.

(*loc. cit.*), to whose paper reference should be made for a description of this salt.

During the present investigation, in one case the analysis of the precipitated salt agreed closely with the formula K_2RuCl_5,H_2O. In this preparation, 8 g. of potassium chloride in 30 c.c. of water were added to a cold solution of 5·63 g. of ruthenium trichloride in 130 c.c., sufficient hydrochloric acid being present to cause the solution to fume when heated on the water-bath [Found : Ru, 27·1; K, 20·8; Cl, 46·5; H_2O (diff.), 5·5. Calc., Ru, 27·1; K, 20·9; Cl, 47·3; H_2O, 4·7%].

In another preparation 2·7 g. of potassium chloride in 8·5 c.c. of water were added to a cold solution of 2 g. of ruthenium trichloride in 40 c.c. of hydrochloric acid (*d* 1·1) which had been kept for 2 days, and a precipitate was obtained of the formula $2K_2RuCl_5,3H_2O$ [Found : Ru, 27·05; Cl, 46·1; K, 20·0; H_2O, 6·8 (diff.). Calc., Ru, 26·5; Cl, 46·1; K, 20·35; H_2O, 7·0%]. Another method for the preparation of this salt, $2K_2RuCl_5,3H_2O$ (Miolati's series), is given below (p. 1047).

Howe's Series.—The salt $2K_2RuCl_5,3H_2O$ (Howe's series) was prepared by three different methods. The details given by Howe are so very incomplete that much time was lost in working out the method of preparation in the following manner. Miolati's salt was first obtained by precipitating ruthenium trichloride in acid solution with potassium chloride. The precipitate (0·75 g.) was dissolved in 75 c.c. of water containing 1 c.c. of strong hydrochloric acid, 75 c.c. of absolute alcohol were added, and the solution was boiled under reflux for 20 minutes, when the colour changed from brown to light yellow. The alcohol was distilled off and the residual solution kept for a week. On evaporation, the salt $2K_2RuCl_5,3H_2O$ (Howe's series) separated in small, black crystals, which dissolved in water, giving a brown solution when concentrated and rose-coloured when very dilute [Found : Ru, 26·7; K, 20·3; Cl, 46·0; H_2O, 7·05 (by combustion). Calc., Ru, 26·5; K, 20·35; Cl, 46·1; H_2O, 7·0%].

(2) It appeared probable that the change from Miolati's series to Howe's series was caused by non-solvated hydrogen ions in accordance with the author's views of the catalytic activity of acids (Briggs, J., 1919, **115**, 278) and that the function of the alcohol was to increase the concentration of the non-solvated hydrogen ions. It was therefore expected that Howe's salt would be formed by boiling Miolati's salt with much acid in the absence of alcohol, and this was found to be the case. Owing, however, to partial oxidation by atmospheric oxygen the method is not suitable for preparing Howe's salt in quantity. A solution of Miolati's salt was boiled under reflux for 4 hours with strong hydrochloric acid

(2 vols.) and the resulting dark brown solution was evaporated to crystallisation. By repeated recrystallisation, the compound $2K_2RuCl_5,3H_2O$ was obtained in a pure condition [Found : Ru, 26·7 ; K, 20·4 ; Cl, 45·9 ; H_2O (diff.), 7·0%].

(3) The most convenient method for the preparation of the compound is by the action of alcohol and hydrochloric acid on a mixture of ruthenium trichloride and potassium chloride. Water (450 c.c.) containing 7 c.c. of strong hydrochloric acid, 450 c.c. of alcohol, 2·8 g. of ruthenium trichloride and 2 g. of potassium chloride was boiled under reflux for 20 minutes. The alcohol was distilled off and the solution was kept for a week, after which it was evaporated to crystallisation on the water-bath [Found : Ru, 26·6 ; K, 20·2 ; Cl, 46·1 ; H_2O (diff.), 7·1%].

If the solution is evaporated immediately after removal of the alcohol, impure products are obtained. For example, in one instance, a substance was formed which appeared to have the formula $K_2RuCl_5,2H_2O$ [Found : Ru, 26·0 ; K, 20·6 ; Cl, 45·1 ; H_2O (diff.), 8·2. Calc., Ru, 25·9 ; K, 19·9 ; Cl, 45·1 ; H_2O, 9·2%]. Several attempts to repeat the preparation of this substance were unsuccessful, but it is clear that more than one compound is present in the freshly-prepared solution.

When the preparation of Miolati's salt, K_2RuCl_5,H_2O, mentioned above, was treated with alcohol and hydrochloric acid, and the solution evaporated immediately after removal of the alcohol, the first crystals consisted of the compound $2K_2RuCl_5,3H_2O$ (Howe's series). The second crop, which was not quite homogeneous, gave Ru, 26·6 ; K, 21·0 ; Cl, 47·2 ; H_2O (diff.), 5·2. K_2RuCl_5,H_2O requires Ru, 27·1 ; K, 20·9 ; Cl, 47·3 ; H_2O, 4·7%. It is therefore possible that in Howe's series there is also a compound, K_2RuCl_5,H_2O, as originally described by Howe.

Oxidation of Howe's Salt by Air.—The compound $2K_2RuCl_5,3H_2O$ was dissolved in water and much hydrochloric acid was added. The solution was heated on the water-bath for several days and air was bubbled through, strong hydrochloric acid being added from time to time to make up the loss due to evaporation. A black, crystalline compound separated which was only sparingly soluble in water to give an intensely brown solution [Found : Ru, 27·6 ; K, 21·4 ; Cl, 48·3 ; H_2O (by combustion), 1·2, 1·1. K_2RuCl_5,K_2RuCl_5OH requires Ru, 27·8 ; K, 21·4 ; Cl, 48·5 ; H_2O, 1·2%]. Attempts were made to determine the valency of the ruthenium in this compound, but a suitable method for this purpose could not be devised.

Action of Chlorine on Howe's Salt.—(1) A 1% solution of the compound $2K_2RuCl_5,3H_2O$ became black when treated with chlorine. After prolonged passage of a current of chlorine, the black colour

disappeared, the solution becoming yellow with a strong odour of ruthenium tetroxide. The black solution gave a precipitate when strong electrolytes such as potassium chloride were added. The black colour was probably due to a colloidal substance, possibly ruthenium tetrahydroxide, which undergoes further oxidation to RuO_4. It should also be observed that, in the presence of very much acid, the compound $2K_2RuCl_5,3H_2O$ (Howe's series) is not blackened by chlorine or bromine. ·

(2) Chlorine was passed for $1\frac{1}{2}$ hours through a cold solution of the salt $2K_2RuCl_5,3H_2O$ (Howe's series) (1·5 g.) in 15 c.c. of water, which was then evaporated in a vacuum over caustic potash and sulphuric acid to dryness. The residue of reddish-brown crystals and greenish-black scales was dissolved in hydrochloric acid and again evaporated in a vacuum to crystallisation. Only the reddish-brown crystals were now obtained [Found : K, 20·4; Ru, 26·65; Cl, 45·9; H_2O (diff.), 7·1. $2K_2RuCl_5,3H_2O$ (Miolati's series) requires K, 20·35; Ru, 26·5; Cl, 46·1; H_2O, 7·0%]. This salt in aqueous solution, unlike the corresponding compound in Howe's series, did not give a black coloration with bromine or chlorine. The colour of the very dilute solution was yellow.

(3) As Howe recommended treatment by chlorine in acid solution to prevent hydrolysis, the following attempt was made to prepare the compound K_2RuCl_6. The triaquodecachloro-dirutheniate, $2K_2RuCl_5,3H_2O$ (Howe's series) (8 g.) was dissolved in 27 c.c. of water and 1 c.c. of strong hydrochloric acid. After chlorination and evaporation, the black solution deposited 1·4 g. of a black, crystalline substance [Found: Ru, 26·7; K, 19·4; Cl, 44·3; $OH+H_2O$ (diff.), 9·6. Calc. for K_2RuCl_5OH,H_2O, Ru, 25·9; K, 19·9; Cl, 45·2; $OH+H_2O$, 8·9. Calc. for K_2RuCl_6, Ru, 25·9; K, 19·9; Cl, 54·2%]. On further evaporation of the solution, crystals of potassium chloride separated mixed with a further quantity of the black compound. The solution was filtered and the filtrate was evaporated to dryness and the residue dissolved in hydrochloric acid. On evaporation in a vacuum, brown crystals were deposited having the formula $2K_2RuCl_5,KRuCl_4,3H_2O$ or $K_5Ru_3Cl_{14},3H_2O$ [Found.: Ru, 29·1; K, 18·7; Cl, 47·25; H_2O (diff.), 4·95. Required: Ru, 29·0; K, 18·6; Cl, 47·2; H_2O, 5·1%].

Note on Ruthenium Tetroxide.

The ruthenium tetroxide obtained by bubbling a current of chlorine through heated sodium rutheniate solution in a retort as described by Howe can be collected by means of an adapter dipping under water contained in a two-necked Woulfe's bottle, a delivery tube from the second neck taking the fumes into an absorption

apparatus filled with aqueous alcoholic potash. The ruthenium tetroxide falls to the bottom of the bottle as a yellow solid which dissolves completely after standing some hours and the solution can then be reduced by pouring into aqueous potash containing alcohol. This method of working is very much more convenient than the method used by Howe.

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CXLVI.—*The Reaction between Aromatic Aldehydes and Phenanthraquinone in presence of Ammonia.*

By ANUKUL CHANDRA SIRCAR and NIRMAL CHANDRA GUHA RAY.

IN presence of ammonia phenanthraquinone condenses with benzaldehyde to form an oxazole derivative and with hydroxy-aldehydes to form iminazoles (Japp and Wilcock, J., 1880, 37, 661; 1881, 39, 225; Japp and Streatfeild, J., 1882, 41, 146):

$$C_{14}H_8 \underset{O}{\overset{N}{\diagdown}} CPh \xleftarrow{\text{PhCHO} + \text{NH}_3} C_{14}H_8O_2 \xrightarrow{\text{OH·C}_6\text{H}_4\text{·CHO} + 2\text{NH}_3}$$

$$C_{14}H_8 \underset{N}{\overset{NH}{\diagdown}} C·C_6H_4·OH.$$
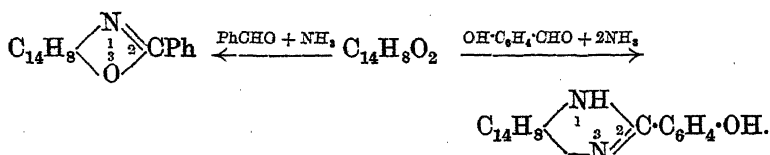
Aromatic nitro- and bromohydroxy-aldehydes also yield iminazoles (Sircar and Sircar, J., 1923, 123, 1559).

When the reaction was applied to acenaphthenequinone, oxazoles were sometimes formed instead of the expected iminazoles (unpublished work). This result led to a study of the action of aromatic aldehydes on phenanthraquinone in presence of ammonia under various conditions and it was found that, although the exact conditions are different for each aldehyde, in general one and the same aldehyde gives an oxazole at a low temperature and an iminazole at a high temperature. The course of the reaction, therefore, is not dependent on the nature of the aldehyde, as was suggested by Japp and Streatfeild (*loc. cit.*).

2-*Phenylphenanthriminazole.*—The product obtained by heating 1 g. of phenanthraquinone, 1 g. of benzaldehyde, and 25 c.c. of strong aqueous ammonia at 160—170° for 4 hours was finely powdered and digested with boiling benzene. The residue crystallised from pyridine in clusters of light yellow needles, not melting below 295°. It was readily soluble in pyridine, nitrobenzene, acetic acid, acetone, or alcohol, slightly soluble in benzene, and produced a blue solution with concentrated sulphuric acid (Found: N, 9·8. $C_{21}H_{14}N_2$ requires N, 9·5%).

2′-Hydroxy-2-phenylphenanthroxazole. — A solution of 1 g. of phenanthraquinone and 1·2 g. of salicylaldehyde in 250 c.c. of warm amyl alcohol was cooled to 10—15° and treated with dry ammonia gas for 15 minutes, the quinone, which had separated on cooling, soon dissolving. The solution was immediately concentrated; the precipitate obtained crystallised from pyridine in colourless needles, m. p. 231—233°. The oxazole is readily soluble in pyridine, nitrobenzene, or acetone, slightly soluble in acetic acid or benzene, insoluble in alcohol, and develops a bluish-green fluorescence with strong sulphuric acid (Found : N, 4·9. $C_{21}H_{13}O_2N$ requires N, 4·5%).

3′-Nitro-2-phenylphenanthroxazole, prepared in the same way as the preceding compound (dry ammonia gas was passed for 20 minutes) from phenanthraquinone (1 g.) and *m*-nitrobenzaldehyde (1·2 g.), crystallised from pyridine in light yellow needles, m. p. 248°. It was insoluble in acetone, slightly soluble in acetic acid, benzene, or alcohol, and readily soluble in pyridine or nitrobenzene. With strong sulphuric acid it developed a greenish-yellow coloration (Found : N, 8·7. $C_{21}H_{12}O_3N_2$ requires N, 8·2%).

2′-Nitro-2-phenylphenanthroxazole, prepared in a similar way from *o*-nitrobenzaldehyde, separated from pyridine in yellow needles, m. p. 166°. It was slightly soluble in alcohol or acetone, soluble in pyridine, nitrobenzene, acetic acid, or benzene, and dissolved in concentrated sulphuric acid with a yellowish-brown colour (Found : N, 8·5. $C_{21}H_{12}O_3N_2$ requires N, 8·2%).

2′-Nitro-2-phenylphenanthriminazole, obtained in the same way as 2-phenylphenanthriminazole (*vide supra*) from *o*-nitrobenzaldehyde (1·2 g.) and phenanthraquinone (1 g.), crystallised from nitrobenzene in light yellow, hexagonal plates.

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CXLVII.—*The Measurement of the Dielectric Constants of Liquids.*

By HERBERT HARRIS.

AN attempt to correlate on a physico-chemical basis certain electrolytic phenomena with the dielectric constants of liquids led to the work embodied in this paper. The existing methods of determining the dielectric constants at telephonic frequencies are open to considerable objection, and the aim of the present paper is to discuss critically and explore experimentally the measurement of the dielectric constants of liquids by alternating current bridge methods.

Methods of Measurement.—The three main methods of determin-

ing the dielectric constants of liquids are : (a) the method which depends upon the frequency of oscillation of a triode valve circuit (Graffunder, *Ann. Phys.*, 1923, **70**, 225; Herweg, *Verh. deut. Phys. Ges.*, 1919, **21**, 272; Grützmacher, *Z. Physik*, 1924, **28**, 342). This method, however, is sensitive only at frequencies of the order of 10^5 to 10^6 cycles per second; (b) the wave-length method, developed by Drude and used extensively by Walden. Some limitations and possibilities of this method have been discussed by Southworth (*Phys. Rev.*, 1924, **23**, 631); (c) alternating current bridge methods, which are the most suitable for telephonic frequencies of 350 to 5000 cycles per second.

The third method is the one which has been used in the present work. In the published papers on the dielectric constants of liquids, of interest to chemists, there is little real understanding of measurements of this kind. It is proposed, therefore, first of all to discuss critically, with due regard to the special difficulties arising in the case of liquids which are not insulators, the alternating current bridge methods which may be employed. For good insulators, the methods are adequately dealt with in several standard works, particularly in Hague's "Alternating Current Bridge Methods," which became available while this investigation was in progress.

Before a proper understanding of the principles underlying bridge methods can be obtained, two points must be carefully considered :—

(i) *The equivalent circuit of an imperfect condenser.* When an alternating current is applied to a perfect condenser, the current vector leads by 90° on the voltage vector. With an imperfect condenser, the angle of lead is reduced by some angle θ, known as the "*loss angle*," which may be taken as a measure of the imperfection. It may vary from a few seconds in the case of a good laboratory standard condenser to nearly 90° in the case of "condensers" with certain liquids as dielectric.

To balance an imperfect condenser, either of the two systems A and B (Fig. 1), composed of perfect condensers K and C and pure resistances R and S, may be adopted. The only object of the resistances is to give the same phase displacement as the imperfect condenser by dissipating, as heat, the same amount of power. It can readily be shown (compare Hartshorn, *J. Brit. Elect. Manuf. Assoc.*, 1923, **13**, 89) that when these two systems are each equivalent to the imperfect condenser, with loss angle θ,

$$\cos^2\theta = C/K.$$

It is to be noticed that $C \neq K$ unless $\cos^2\theta = 1$, that is, unless θ is negligibly small. Therefore the capacity of a condenser, with an appreciable loss angle, possesses two values, which, apparently, have exactly similar claims to being regarded as correct. Since, however,

the capacity determined by the parallel resistance method yields values of the dielectric constant in agreement with values determined by other methods, it is natural to give preference to this system of measurement.

(ii) *Earth capacities.* In defining the capacity of a simple condenser the influence of neighbouring bodies is usually neglected. It is of practical importance to analyse the capacity distribution when more than two conductors are involved.

In the case of a shielded air condenser, having a pair of electrodes insulated from and surrounded by an earthed metallic screen, as in Fig. 2A, it can be shown that

$$C = C_{12} + C_1 C_2 / (C_1 + C_2)$$

where C is the apparent capacity between the electrodes, C_{12} is the intercapacity between the electrodes, and C_1 and C_2 are the earth capacities of the two electrodes (compare Fig. 2B) (for details, see Hague, *op. cit.*, or " Dictionary of Applied Physics," edited by Glazebrook, 1924, Vol. II., p. 103).

The special importance of the above analysis arises from the fact that, by introducing a liquid (D.C. $= \epsilon$) as dielectric, it will not always be possible to write the new capacity, C', of the condenser as $C' = \epsilon C$; it may be more accurate to write

$$C' = \epsilon C_{12} + C_1 C_2 / (C_1 + C_2)$$

or C_1 and C_2 may be slightly affected; the change will depend upon the geometrical arrangement of the conductors.

Thus, in the bridge set-up, special attention must be directed to the design of the condenser, and also to the method by which it is inserted in the bridge.

Series Resistance Method.—Apparently the simplest method of determining capacity is by the bridge introduced by De Sauty and applied to alternating current measurements by Wien (*Ann. Physik*, 1891, 44, 697). In practice, however, the bridge is almost useless, because sharp balance cannot be attained, no measures being adopted to balance the imperfections of the condenser.

Modifications of the De Sauty method have therefore been adopted to neutralise the condenser leaks. In one of the simplest, a variable resistance is placed in series with the condenser with the smaller loss angle; but it is of little importance when dealing with liquids which behave as poor dielectrics, such as chloroform, nitrobenzene, acetone, etc. For example, in the case of chloroform, θ is of the order of $24\frac{1}{2}°$; if C (refer to system B, Fig. 1) $= 0,00100$ microfarad, then $K = 0,00152$ microfarad. Again, for commercial acetone, with $\theta = ca.\ 89\frac{1}{2}°$, and $C = 0,00100$, $K = 13$ microfarads, which would be an absurd value to take, because it would correspond to a dielectric constant of approximately 260,000.

Fig. 1.

SYSTEM A.

SYSTEM B.

Fig. 2A

Fig. 2B

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

1052
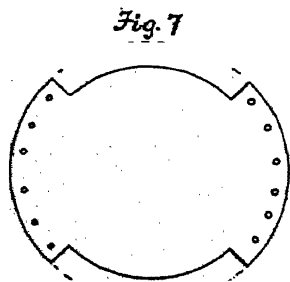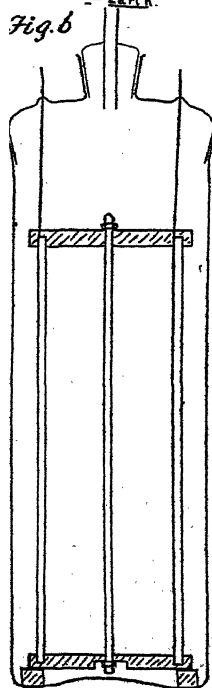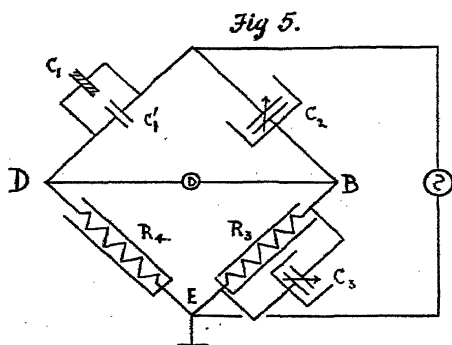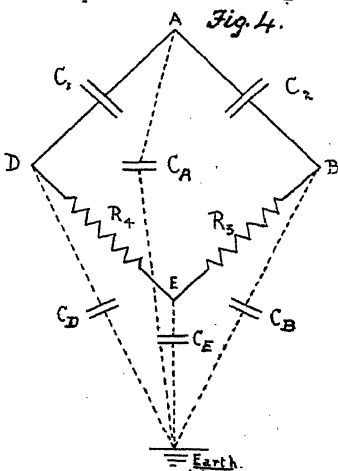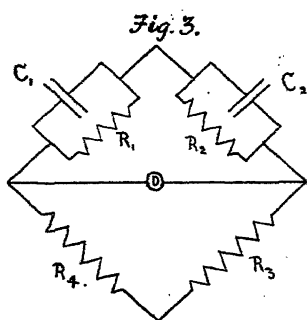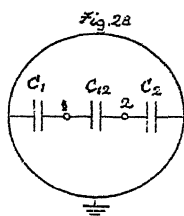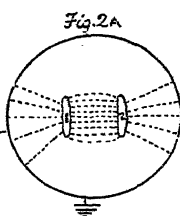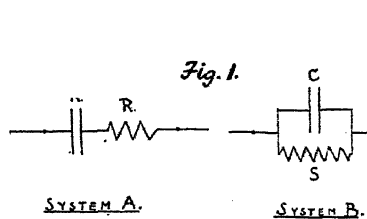
It is realised immediately that this method is restricted to liquids with very high insulating powers, such as benzene and carbon tetrachloride, in which cases very satisfactory results may be obtained.

Parallel Resistance Method.—This is the method most frequently used, and is easily understood by reference to Fig. 3; the condenser leak is balanced by a resistance in parallel with the standard condenser.

This method is the only one possible when the dielectric possesses a large loss angle, for instance, chloroform, ethylene dichloride, etc. With good dielectrics the method can still be used, but in order to overcome the difficulty of using very high resistances in parallel with the standard condenser, both condensers have to be shunted by suitable resistances. But this plan is not to be recommended because, by so doing, an appreciable quantity of the current passes through the resistances, thus reducing the sensitivity of the condenser setting.

The series resistance method, therefore, is the better when dealing with dielectrics characterised by small loss angles, and the parallel resistance method is used when the loss angle increases. The limit of the method is determined by the sensitivity of the condenser setting.

Earth Capacities; Their Effect on the Bridge.—Before passing to the description of the Schering and Semm's bridge, it will be convenient to discuss the effects of earth capacities on the bridge.

As is well known, every portion of a conductor has a capacity to earth, so that in any bridge set-up this capacity is distributed continuously along every arm. Giebe, however, has shown that, to a near approximation, the total effect of this distribution can be represented by four capacities from the four corners of the bridge to earth, represented in Fig. 4 by the dotted construction. This approximation is not justified in the case of bridges where the arms contain such things as high resistances, in which there are distributed capacities of considerable magnitude.

From the figure, it is clear that the arm AD is not composed solely of the condenser C_1, but C_1 and a combination of C_A and C_D. Actually the capacity of the arm can be written as $C_1 + C_A C_D/(C_A + C_D)$. Similarly, the effective capacity of the arm AB is $C_2 + C_A C_B/(C_A + C_B)$, the impedance of the arm DE is $1/\{1/R_4 + jwC_D C_E/(C_D + C_E)\}$, and the impedance of the arm BE is $1/\{1/R_3 + jwC_B C_E/(C_B + C_E)\}$. Therefore, the impedances of the arms have to be corrected for these earth capacities.

There is also a further effect due to earth capacities. In the bridge, a telephone is placed across the points D and B. Now the observer being at earth potential and D and B being at some other potential, there will be a leak from the bridge, through the observer, to earth,

giving rise to what is known as the " head effect " of the observer. These difficulties can be overcome very ingeniously by Wagner's earthing device (*Elektr. Z.*, 1911, **32**, 1001; 1912, **33**, 635). A detailed description is given by Hartshorn (*loc. cit.*) and by Hague (*op. cit.*).

The use of the Wagner earthing device would make the measurements very much more difficult. It is quite difficult to obtain a well-defined minimum when only one arm has to be adjusted, and if it were necessary to balance a subsidiary arm and then the bridge arm, and repeat this process until satisfactory balance is obtained for both arms, the time so spent would be sufficient for the power, dissipated as heat in the experimental condenser, to cause a marked rise in the temperature of the dielectric. The difficulty has therefore been overcome by using the device of Monash (see later), which, though not so sound theoretically, offers, in this case, considerable practical advantages over the arrangement of Wagner.

Schering and Semm's Bridge.—This method, suggested by Schering (*Z. Instrum.*, 1920, **40**, 124), and actually first used by Semm (*Arch. Elektr.*, 1920, **9**, 30), was primarily designed for high voltage work, but Giebe and Zickner (*ibid.*, 1922, **11**, 109) have used it in an exceedingly accurate investigation, in which they measured the loss angles of standard condensers (of the order of 1″) (see also Hartshorn, *Proc. Physical Soc.*, 1924, **36**, 399).

The method is limited in application to liquids which possess a fairly small loss angle, but for such liquids (benzene, carbon tetrachloride, etc.) it is by far the most satisfactory.

The principle of the method is illustrated by Fig. 5. The shaded condenser, C_1, is the one to be measured; its capacity is measured on the condenser C_2, the ratio arms being the resistances R_3 and R_4.

Before perfect balance is obtained in any alternating current bridge not only must the two detector terminals be at the same potential, but the voltages at the two points must also be in phase. In all the bridges previously dealt with, the phase difference has been rectified by a resistance in parallel, or in series with the standard condenser. In Schering and Semm's bridge, this has been accomplished by placing a variable condenser across the resistance R_3. It can be shown that when such a bridge is balanced, $\rho_1 = C_3/C_2 \cdot R_4$ (where ρ_1 is the equivalent series resistance of condenser C_1) and $C_1/C_2 = R_3/R_4$.

A second point is to be noted. One sees that the point E is earthed. Now the resistances R_3 and R_4 are made very small— in these experiments 1000-ohm coils are used—the result, therefore, is that the drop in potential across the resistances is only a small fraction of the drop across the condensers (whose impedance is approximately 150,000 ohms). Therefore the potentials at the

points D and B are nearly at earth value, and thus the effect of earth capacities in the bridge and the head effect are eliminated. This device due to Monash (*Electrician*, 1907, **59**, 416, 460, 504), was used in all the experiments in this investigation, even when the parallel resistance method was employed.

The method of shielding the apparatus from outside disturbances, to which particular attention must be paid, is indicated in the figure. The aim has been to maintain every screen at or near earth potential; thus the two screens shielding the resistances are directly earthed and the condenser screen is connected to the point B, which, as has been said, is nearly at earth potential.

Since, in general, the rotating plates of the condenser are connected to the screen, it is obvious that the method of screening adopted tends to reduce the effect of the hand capacity when the condenser is adjusted by hand. As a matter of fact, a bridge so screened is very insensitive to outside capacities.

The construction of the experimental condenser will be discussed later.

Apparatus.—The generator. The development of the triode valve has resulted in a valve generator which is entirely satisfactory for the purpose in hand. The valve generator was made by the Cambridge and Paul Company, and has the following features :— (1) It supplies a pure sine-wave current of constant frequency. (2) Its frequency can be adjusted to any value between 50 and 5000 cycles per second by altering the value of the capacity unit. (3) It requires little attention. (4) One set of windings is suitable for high impedance bridges. (5) Between the primary and secondary windings there is a screen, which by connecting to earth prevents direct interference of the generator on the bridge.

The frequency of the generator was calibrated against two König tuning forks (frequencies 1024 and 2048). The frequency was given by the formula $n = a/\sqrt{C}$, where a is a constant and C the value of the capacity unit.

Another tuning fork, frequency about 890, was then calibrated against the generator, and its frequency thus determined served as a test of the generator frequency from week to week. Little variation was observed. In every experiment the generator was adjusted so that it gave a frequency of 1000 cycles per second.

The detector. The necessity for an accurate setting of the frequency of the generator is to ensure maximum sensitivity being obtained. Since a telephone (made by Brown) sensitive at 1000 cycles per second was used as detector and since in the sensitivity–frequency curve for a telephone of this description there is a very sharp peak, it becomes evident why strict attention was paid to this point. It

may be taken as a general rule that a given telephone is at least three times as sensitive at its resonance frequency as at any other.

There is one other point to be noted about the detector: for maximum sensitivity, a high impedance bridge requires a high impedance detector. It was accordingly found that a 1000-ohm telephone was far more sensitive than a similar 120-ohm one, and the former was therefore used.

The ratio arms. It has been seen that, in general, the ratio arms are two resistances. In the Fleming and Dyke bridge, two condensers are used. The advantage of this method is that it is fairly easy to construct the condensers with small residuals, whereas with large resistances the residuals become important. Nernst and his co-workers (Nernst, *Z. physikal. Chem.*, 1894, **14**, 622; Philip, *ibid.*, 1897, **24**, 18; Turner, *ibid.*, 1900, **35**, 385), together with many recent workers in this field, have used liquid resistances, mannitol–boric acid solution. Two points are to be noted regarding such resistances. The platinum electrodes must be thickly platinised, so as to reduce to a minimum their residual capacity, due, for instance, to polarisation capacity. On the second point, I wish merely to state my own experience, namely, that it was not found possible to maintain constant the ratio of the two resistances, constructed according to Turner's directions.

It must nevertheless be conceded that the introduction by Nernst of liquid resistances of, say, 20,000 ohms with very small residual capacity, possibly one or two micro-microfarads, was an immense improvement on the large coils of wire, with large residuals, that would otherwise have been needed.

Since, however, in these experiments only comparatively small resistances were required, the ratio arms were specially obtained. They were two 1000-ohm coils, guaranteed to within 0·02% ohmic accuracy, made by H. W. Sullivan. They are the so-called non-reactive coils, possessing very small residuals; they are further guaranteed to be equal to each other with an accuracy of 0·01%.

The standard condenser. Undoubtedly the most important portion of the bridge is the measuring instrument, that is, the standard condenser. This condenser should have the following properties :—
(1) it should be a true condenser, that is, the current taken by it when a sinusoidal potential difference is applied should lead on the potential difference by $\pi/2$ and should be free from harmonics; (2) it should be free from losses and absorption effects in the dielectric; (3) the capacity should be definite and permanent; (4) the capacity should be independent of the frequency, wave-form, and temperature.

Given this set of conditions, it is possible to use only air or mica

as the dielectric material. " Other materials are only used where capacitance is required without the advantages of permanence, accuracy, and perfection " (Hague, *op. cit.*).

The condenser used in this investigation was a laboratory standard air condenser, made by H. W. Sullivan, and fitted with a vernier and lens. The maximum capacity was about 1200 $\mu\mu$f., and the scale was divided into degrees, being read to 0·1° by means of the vernier. 0·1°, or 1 unit, was equal to 0·700 $\mu\mu$f. In this paper, all the capacities are quoted in these units, unless otherwise stated. Thus a capacity of 100 will mean a capacity of 100 × 0·700 $\mu\mu$f. = 70 $\mu\mu$f.

The calibration of the condenser was furnished by the maker, and over the range used the capacity was a linear function of the scale reading.

With the bridge correctly balanced, the condenser can be set to less than 0·700 $\mu\mu$f. Indeed, with such liquids as benzene, an enlarged scale would certainly be an advantage, because the setting of the condenser is so well defined. There would be little difficulty in setting the bridge to within 0·1 $\mu\mu$f. with a capacity of 1000 $\mu\mu$f.

Criticism of the Nernst Method.—A considerable amount of time was initially spent with a bridge constructed from apparatus of the Nernst-Turner type. In view of the importance attached by chemists to Turner's investigation (see, *e.g.*, Richards and Shipley, *J. Amer. Chem. Soc.*, 1919, **41**, 2002), it may be of value to subject it to a critical examination, for in the author's judgment the accuracy of the method is open to question.

(1) Apart from the fact that the Nernst interrupter does not meet modern requirements, the Nernst-Turner type of condenser, which has been used by many workers (see, *e.g.*, Hertwig, *Ann. Physik*, 1913, **42**, 1099; Joachim, *ibid.*, 1919, **60**, 570; Harrington, *Physical Rev.*, 1916, **8**, 581; Richards and Shipley, *loc. cit.*), does not behave as a true condenser, *i.e.*, the current does not lead on the voltage by $\pi/2$ when a sinusoidal potential difference is applied. This must be so, because glass possesses a relatively large loss angle, and when the condenser is balanced against a perfect condenser an appreciable resistance must be used to rectify the phase displacement. With the Schering and Semm's bridge, used in these experiments, the maximum value of the condenser C_3 (Fig. 5) is 0·001 microfarad, and the resistances are 1000 ohms each. With this bridge it is not possible to balance the Nernst-Turner condenser, although with the same arrangement a benzene condenser of at least twice the capacity has been accurately balanced. From this observation it follows that, if the dielectric constant of benzene were being determined by the method of Turner, *the measuring condenser would have a much greater loss angle than the condenser to be measured.*

Further, Thornton (*Proc. Physical. Soc.*, 1912, **24**, 301), studying the behaviour of dielectrics, when placed in an alternating current field, by means of an oscillograph, has shown that glass is not only an imperfect dielectric in so far as it reduces the current lead, but also distorts the current wave. In such a case, it is impossible to find any combination of a perfect condenser and a resistance which will produce the same effect. This means that, when used in a bridge, the glass condenser cannot be accurately balanced.

(2) The capacity of the condenser cannot be said to be definite and permanent. The condenser permits of slight lateral displacements involving changes of capacity without change of the scale reading.

(3) The capacity cannot be taken as independent of the temperature, and of this Turner was aware, because he made special determinations of the temperature coefficient of his apparatus.

(4) Further, the use of the Nernst-Turner condenser involves the sliding of the glass plates between the brass plates, and during the process the dust particles that inevitably collect on the top edges of the glass plates form a ridge across the brass plates and thus create a shunt across the condenser, greatly increasing the loss angle. If this minute ridge is brushed away, one notices a distinct improvement in the loss angle.

(5) In the Nernst method electrolytic resistances, consisting of platinum electrodes in Magnanini's solution, are employed. The author found it impossible to maintain their resistance ratio constant, even although the special advantage of Magnanini's solution is that its resistance possesses a small temperature coefficient.

In the following tables are set out the results of experiments in which the two resistances formed two arms of a bridge, a Leeds and Northrup conductivity bridge wire (drum type) forming the other two arms.

Resistances about 2,000 ohms.				Resistances about 15,000 ohms.		
Time (mins.).	Temp. of room.	Bridge reading.	Ratio of the two resistances.	Time (hrs.).	Bridge reading.	Ratio of the two resistances.
0	9·7°	497·15	0·9887	0	496·6	1·0137
15	10·05	498·2	0·9928	¼	496·6	1·0137
30	10·7	498·9	0·9956	1¼	496·5	1·0141
45	10·9	499·5	0·9980	2¼	496·4	1·0145
60	11·5	500·2	1·0008	3¼	496·4	1·0145
				8¾	497·5	1·0101
				24¾	498·3	1·0068
				—	498·2	1·0072
				32¾	498·0	1·0080
				36¼	497·6	1·0090
				38¼	497·5	1·0101

With such resistances it is not possible to obtain very accurate results and therefore they were discarded.

(6) In Turner's investigation no attention seems to have been

paid to the influence of earth capacities on the bridge. Such effects were very marked, for it is stated that slight movements of the observer caused an appreciable shift in the position of balance, and Turner insists on the observer maintaining a constant position with respect to the apparatus. This, in itself, is proof that large earth capacities were affecting the bridge. In a bridge of the type used, the only method of successfully ensuring the correctness of the minima is to use a Wagner earthing device.

It might be noted, too, that Turner, in some of his experiments, placed his dielectric trough in a massive piece of brass, in order to reduce any temperature variations. This seems to be open to criticism, because the earth capacity of the metal must have quite a considerable value.

Description of the Bridge Set-up.

(a) *Direct action between the generator and the bridge and the telephone.* The valve generator was placed about 6 feet from the bridge itself and about 14 feet from the telephone. At these distances there was no direct inductive action between the generator and the bridge, and no capacity effects were introduced, because reversal of the connexions to the generator caused no change in the balance point. The action of the generator on the telephone was very small, reversal of the telephone connexions causing only a negligible change in the reading.

(b) *Loose connexions in the bridge.* The connexions at the points D, B and A (Fig. 5) were made with mercury cups in ebonite, screwed to the bench. All bad contacts were thus eliminated, and, since the bridge was symmetrical with respect to the cups, no unbalanced capacity was introduced.

(c) *The insulation of the bridge* received particular attention. All the apparatus which was not provided with screens, *e.g.*, the leads, was supported on ebonite stands about 2 inches from the bench. Such insulation is of particular importance in all high impedance bridges.

(d) *The condenser* C_3, made by Gambrell, had a maximum capacity of 0·001 microfarad. The condenser C_1' was a small Murdoch condenser, maximum capacity 0·0005 microfarad, which was set so that the "zero" of all readings on the standard condenser was a point on the "straight line portion" of its capacity. The capacity to be measured was inserted across this small condenser and the increase in capacity was the capacity required.

(e) *Correction due to the capacity of the leads.* The two leads which connect the experimental condenser to the bridge cannot be balanced by "dummy" leads. Thus a small correction has to be applied to the value of the capacity as above measured. This correction

is obtained by noting the increase in capacity when the container of the experimental condenser and the leads, but minus the condenser itself, are inserted in the bridge.   This correction was about 1·5 units or about $1\mu\mu f$. and was determined for every container used.

(*f*) *Earth capacity and motion of the observer.* The movement of the observer had very little effect on the position of the bridge setting. This was taken to be substantial evidence that the bridge was well screened and that errors due to earth capacities were negligible. But in every case the observer was 6 feet or so from the bridge, the condenser being operated by a long wooden arm from that distance.

(*g*) *The insertion of the experimental condenser.* As will be seen later, the experimental condensers consisted of two concentric metal cylinders contained in a glass vessel. The point here empha- sised is that the outer cylinder is connected to the point D of the bridge and the inner cylinder to the point A. The outer cylinder, which also serves as a screen to the inner one, is thus connected to a point practically at earth potential, so that the working capacity of the condenser is actually the capacity between the two plates, that is, C_{12}.

(*h*) *Temperature control.* The experimental condenser was placed in an electrically heated and controlled thermostat, which main- tained the temperature at 25·00° with a variation of less than 0·01°. Whenever a reading was being taken, the electric heater was disconnected from the supply main.

(*i*) *Correction due to the capacity of the parallel resistance.* In the case of liquids with large loss angles, where the use of Schering and Semm's bridge was not possible, the condenser C_3 (Fig. 5) was removed by disconnecting from the bridge, at B, and earthing both terminals, and the parallel resistance method was employed. The liquid resistances were similar to those used by Turner, being varied by the movement of conical plungers. In these experiments, a resistance has to be inserted across the measuring condenser to balance the imperfections of the experimental condenser. This resistance must obviously have a small residual capacity, which must be corrected. For this purpose, the resistance is placed in the opposite side of the bridge and the bridge is balanced by means of a second similar resistance. The first resistance is then removed, and the bridge again balanced. The difference in the two capacity settings, which is generally of the order of 3 or 4 micro-microfarads, may be taken as the residual capacity of the resistance. The only assumption made in this method of correction is that the residual capacity of the second resistance does not vary when the plunger is moved.

This method has been adopted in preference to putting two resistances (permanently) in opposite arms of the bridge, as is

so frequently done, because in the method adopted one gets the maximum sensitivity obtainable.

(*j*) *Schering and Semm's bridge for zero balance.* In the large number of cases where the parallel resistance method was used, the zero setting of the bridge would have been troublesome because, the small Murdoch condenser C_1' having a much larger loss angle than the measuring condenser, perfect balance would not have been immediately attainable. To obtain such a balance readily, Schering and Semm's bridge, involving the use of the condenser C_3, was employed and when the zero setting had been obtained the condenser C_3 was again earthed. This is a considerable improvement on previous methods of working.

(*k*) *The minima.* In all the experiments exceptionally good minima were obtained, the telephone being quite silent. For good work, perfect quietness is essential.

(*l*) All the results have been calculated on the assumption that polarisation capacities in the experimental condenser are absent. It is an assumption always made in this type of work, but it could only be proved by experiment.

The Experimental Condensers.—A series of condensers was constructed so that maximum accuracy could be secured. If the maximum capacity that can be measured is 1200 $\mu\mu$f., a condenser containing nitrobenzene as dielectric must have an air capacity of about $1200/35 = 35 \mu\mu$f., and with benzene as dielectric, a capacity of about 70 $\mu\mu$f. Since the dielectric constant of nitrobenzene is the ratio of two capacities, if nitrobenzene is standardised against benzene, the experimental value $2 \times 1200/70$ will be obtained. The accuracy of this expression, being determined by that with which the capacity 70 $\mu\mu$f. is measured, is poor. It is clear, therefore, that a standard series of liquids with increasing dielectric constant must be obtained in order that any condenser may be accurately standardised. The method adopted was to measure the dielectric constant of benzene against air, that of chloroform against benzene, that of ethylene dichloride against chloroform, and so on, the smallest capacity measured thus being 400 $\mu\mu$f.

The requisite condensers were all constructed on the following principle. Two concentric brass cylinders were supported in compressed fibre end-pieces, grooved to take the cylinders at a " push fit." The end-pieces were bolted together as indicated in Fig. 6, and the whole was placed on a fibre ring in a stoppered glass container. The leads were soldered to platinum wires, which were sealed through the stopper and were there soldered to the leads to the bridge. Through an orifice in the stopper the liquid was poured in when the condenser was assembled. The stopper of the orifice was provided with a tube and tap (not shown in the figure), by which

the condenser vessel could be evacuated and any air bubbles trapped between the condenser plates removed. To facilitate this removal small holes were bored through the fibre end-pieces so that the space between the condenser plates had direct communication with the outer space. The dimensions will be given later.

Method of Calculating the Dielectric Constant.

In all the measurements recorded in this work, a correction has to be applied for that portion of the capacity of the condenser which is influenced by the fibre end-pieces.

With air as dielectric, the capacity, measured across the terminals of the two condenser leads, is composed of two parts, viz., that due to air as dielectric, x, and that caused by the fibre end-pieces, y. If a liquid, say, benzene, is introduced, the capacity is still composed of two parts, viz., that due to benzene as dielectric, ϵx (where ϵ is the dielectric constant of benzene), and y. It would thus appear that a constant quantity, y, has been added to the two capacities whose ratio gives the dielectric constant of benzene. Thus are obtained the two equations

$$x + y = a \text{ and } \epsilon x + y = b,$$

where a and b are determined experimentally.

After these readings have been taken, the fibre end-pieces can be cut (as shown in Fig. 7) so that they cover only half the rim of the condenser, the capacity due to the fibre end-pieces thus being exactly halved. With this new condenser, two equations are again obtained,

$$x' + \tfrac{1}{2}y = c \text{ and } \epsilon x' + \tfrac{1}{2}y = d,$$

where x' is the value corresponding to x, for the second condenser. From these four equations, the four unknown quantities x, y, x', and ϵ can be determined.

A little thought, however, will show that this view is not quite correct. The objection is, that y is not constant.

With air as dielectric (D.C. = 1), there will be a certain crowding of the lines of force into the fibre end-pieces (D.C. = 3·5), giving rise to the capacity due to the end-pieces. When benzene is used as dielectric, there will not be the same crowding of the lines of force at the interface between the fibre and the dielectric, because the difference in the two values of the dielectric constants is not so great as previously, and therefore the capacity of the end-pieces is somewhat reduced.

The method of attack adopted is somewhat arbitrary, but the result was tested in the case of benzene and was found to be satisfactory. With the full end-pieces on the condenser, the ratio of the capacities of the condenser, measured in air and in benzene, is z_1. With half the end-pieces, this ratio is slightly increased to a value z_2.

It is assumed that if the remaining halves of the end-pieces could be removed, the second increase in the ratio would be the same as the first. The dielectric constant of benzene is therefore calculated as

$$z_1 + 2(z_2 - z_1) \text{ or } z_2 + (z_2 - z_1).$$

Justification for this procedure was obtained experimentally. A new condenser was constructed exactly similar to the first except that its length was reduced to a quarter of the previous value, and its air capacity was measured. Subtraction of this capacity from the air capacity of the larger condenser gives the capacity, due to air as dielectric, of a " virtual condenser " without any end interference. This being repeated with benzene as dielectric in the two cases, the difference now gives the capacity of the same " virtual condenser " with benzene as its dielectric. The ratio of these two quantities must be the true dielectric constant of benzene.

For benzene, the two methods gave the same value for the dielectric constant, viz., 2·2482 ± 0·0003 and 2·2488 ± 0·0005.

The probable errors of the means (see Tables) have been calculated by the method of " least squares." The author is aware that a detailed analysis of the results would show inconsistencies, but wishes the probable errors given to be taken as indicating the order of accuracy of the final results.

Purification of Materials.

Benzene. Commercial benzene was shaken successively with concentrated sulphuric acid, water, and distilled mercury to remove thiophen, sulphuric acid, and any sulphur compounds respectively. The filtered liquid was washed with water, dried over calcium chloride, fractionally distilled, and thoroughly dried over sodium wire (Richards and Shipley, *J. Amer. Chem. Soc.*, 1914, **36**, 1825; 1919, **41**, 2002). It distilled within a range of 0·02°.

Carbon tetrachloride, obtained from the British Drug Houses, was dried with calcium chloride and fractionally distilled, the bulk passing over within a range of less than 0·1°.

Chloroform (A.R.) was shaken once with sodium bisulphite solution, twice with water, and thrice with concentrated sulphuric acid. After being thoroughly washed with water, it was dried over calcium chloride and fractionally distilled through a moderately efficient column (Richards and Camm, *J. Amer. Chem. Soc.*, 1921, **43**, 827; Schoorl and Regenbogen, *Rec. trav. chim.*, 1922, **41**, 1). The b. p. of the resultant fraction was constant to within 0·03°. If carbonyl chloride is formed by the action of light, it is readily detected by the change in the odour of the chloroform, and may be removed by shaking with solid sodium hydroxide. To ensure uniformity of the chloroform samples used throughout the lengthy series of experi-

ments, every sample was tested, the criterion of uniformity or purity being the refractive index. The values of $n_D^{25^\circ}$ observed for the several samples were 1·4433, 1·4433, 1·44326, 1·44321, 1·44329, 1·44327, 1·44319, 1·44331.

Ethylene dichloride, obtained from the British Drug Houses, was shaken with concentrated sulphuric acid and with water, and then with potassium hydroxide for 2 days. It was again washed with water, dried over calcium chloride, and fractionally distilled through an efficient Young's column (Worley, J., 1914, **105**, 273; Timmermans, *Bull. Soc. Chim. Belg.*, 1910, **24**, 246). After three distillations, there was no improvement in the b. p. (83·0—83·3°) or refractive index. The values of $n_D^{17^\circ}$ of the several samples were 1·44197, 1·44205, 1·44211, 1·44211, 1·44215.

o-Nitrotoluene (Kahlbaum) was distilled several times under reduced pressure, the first and last fractions being rejected. It was then dried by shaking with phosphorus pentoxide for 30 hours, and after filtration was twice distilled under reduced pressure (25 mm.). Moisture appears to have a large effect on the dielectric constant. The values of $n_D^{25^\circ}$ for the several samples used were 1·54418, 1·54442, 1·54421.

Nitrobenzene (purified) was left standing for several days with bromine. The bromine was then removed with dilute caustic soda solution, and the nitrobenzene washed with water, dried over calcium chloride, and distilled. The middle fraction, comprising more than 90% of the whole, remained unchanged in b. p. (range within 0·1°) and refractive index ($n_D^{25^\circ}$ 1·55006) after several redistillations. It was then shaken for several days with freshly prepared silver oxide (dried at the ordinary temperature), dried over phosphoric oxide, and distilled under about 20 mm. pressure (Bruner and Galecki, *Z. physikal. Chem.*, 1913, **84**, 513).

TABLE I.

Data upon Condensers Used.

No.	End.	Length (cm.).	Extl. diam. of inner cyl. (cm.).	Int. diam. of outer cyl. (cm.).	Dielectrics used.
1	Whole.	20	5·9	6·1	Air; C_6H_6; CCl_4.
2	Half.	20	5·9	6·1	Air; C_6H_6.
3	Half.	5	5·9	6·1	" "
7	Whole.	30	3·8	4·1	C_6H_6; $CHCl_3$.
8	Half.	30	3·8	4·1	" "
9	Whole.	19	1·8	2·1	$CHCl_3$; $C_2H_4Cl_2$.
10	Half.	19	1·8	2·1	" "
12	Whole.	14·8	1·8	2·3	$C_2H_4Cl_2$; $o\text{-}C_7H_7\cdot NO_2$.
13	Half.	14·8	1·8	2·3	" "
14	Whole.	11·8	2·15	2·8	$o\text{-}C_7H_7\cdot NO_2$; $C_6H_5\cdot NO_2$.
15	Half.	11·8	2·15	2·8	" "

TABLE II.

Dielectric Constant of Benzene.

(Normal " Half-end " Correction Method.)

Bridge : Schering and Semm's.   Frequency : 1000 cycles per second.
Temperature : 25·00° ± <0·01°.

D.C. of benzene.

Con-denser No.	Capacity.		Apparent D.C.	End corr.	Corrected. Air = 1.	True. Air = 1·0006
	Air.	Benzene.				
1	597	1322·5	2·2153	0·0308	2·2461	2·2474
,,	594·5	1317·5	2·2161	,,	2·2469	2·2482
,,	591	1310·2	2·2169	,,	2·2477	2·2490
		Mean	2·2161			
	589·5	1316	2·2324	0·0154	2·2478	2·2491
	588·5	1312·5	2·2302	,,	2·2456	2·2469
	588·5	1313·5	2·2320	,,	2·2474	2·2487
		Mean	2·2315		Mean	2·2482
					Probable error ±0·0003	

* This value is the mean of the following values : 1·00065 (Wagstaff), 1·00065 (Gill), 1·00060 (Carman and Lorance), 1·00054 (Fritts), 1·0005 (Boltzman), 1·0005 (Klemencie).

TABLE III.

Dielectric Constant of Benzene.

(Virtual Condenser Method.)

Condenser No.	Capacity.		Capacity of virtual condenser.		D.C. of benzene (air = 1·0006).
	Air.	Benzene.	Air.	Benzene.	
3	101·5	220·5	487·25	1095·6	2·2498
	102·5	219·5	486·25	1092·1	2·2473
	102·75	221·25	486·25	1093·1	2·2493
Means	102·25	220·4		Mean	2·2488
				Probable error ± 0·0005	

Note.—The capacities of the virtual condenser are obtained by subtraction of the mean capacities for condenser 3 from the appropriate capacities of condenser 2.

TABLE IV.

Dielectric Constant of Carbon Tetrachloride.

Bridge : Schering and Semm's.   Frequency : 1000 cycles per second.
Temperature : 25·00° ± 0·01°.

Condenser No.	Capacity.		Apparent D.C.
	Air.	CCl₄.	
1	589·25	1290·1	2·1894
	590	1289·3	2·1853
		Mean	2·1873

Whence, assuming the relation of true to apparent D.C. to be the same (in the same condenser) for carbon tetrachloride as for benzene, the true dielectric constant of carbon tetrachloride = $2 \cdot 1873 \times 2 \cdot 2482/2 \cdot 2161 = 2 \cdot 219 \pm 0 \cdot 002$.

The arithmetical process adopted in the following tables needs some explanation.   The condensers having been calibrated with a liquid of known dielectric constant, their capacities with other

liquids as dielectrics were observed. On repeating the calibration no change in the condenser was ever observed. Every capacity figure given in the tables is the mean of a series (at least four) of concordant observations. In calculating the apparent dielectric constant, the individual capacity figures of the condenser with the liquid of unknown dielectric constant as dielectric have been divided by the *mean* capacity figure of the condenser with the standard liquid as dielectric, and then multiplied by the known dielectric constant of the latter liquid. This method enables the " probable error " to be calculated in a satisfactory manner.

To obtain the results set out in the following tables, the parallel resistance method was employed, the frequency being 1000 cycles per second and the temperature of the dielectric 25·00° ± <0·01°.

TABLE V.

Dielectric Constant of Chloroform.

The parallel resistance was of the order of 325 × 10³ ohms across a condenser of capacity 1096 μμf., whence the loss angle characteristic of the liquid is approximately 24°

	Condenser No. 7. Capacity.			Condenser No. 8. Capacity.	
Benzene.	CHCl₃.	Apparent D.C.	Benzene.	CHCl₃.	Apparent D.C.
719	1472·25	4·6059	712·8	1465·75	4·6230
719	1471·5	4·6031	713·25	1463·25	4·6152
718·5	1466	4·5859	712·5	1464·5	4·6191
718·25	1465·5	4·5844	712·5	1464·25	4·6183
	1468·8	4·5946	712·95	1464·05	4·6178
	1469·7	4·5975		1462·75	4·6136
	1467	4·5890			
	1467·5	4·5906			
Means 718·7		4·5937	712·8		4·6178

The correction to be applied to these values is 0·0478 for condenser 7 and 0·0239 for condenser 8. The true dielectric constant of chloroform is therefore 4·6417 ± 0·001.

TABLE VI.

Dielectric Constant of Ethylene Dichloride.

Parallel resistance, about 232 × 10³ ohms; capacity, 905 μμf.; whence the loss angle is approximately 35°

	Condenser No. 9. Capacity.			Condenser No. 10. Capacity.	
CHCl₃.	C₂H₄Cl₂.	Apparent D.C.	CHCl₃.	C₂H₄Cl₂.	Apparent D.C.
646·75	1390	10·003	643	1396·3	10·068
645·45	1391	10·011	643	1396·65	10·071
644·05	1392·3	10·019	643	1397·75	10·079
644·3	1391·75	10·016	643·5	1396·5	10·072
645	1391·5	10·014	643·75		
644·5	1391	10·011	644		
644·5	1392·1	10·018	645		
645·5	1391·75	10·016	644·75		
Means 645·0		10·0135	643·75		10·0725

Correction : 0·118 for condenser 9 and 0·059 for condenser 10. Whence the true dielectric constant of ethylene dichloride is 10·131 ± 0·001.

TABLE VII.

Dielectric Constant of o-Nitrotoluene.

Condenser No. 12.			Condenser No. 13.		
Capacity.		Apparent D.C.	Capacity.		Apparent D.C.
$C_2H_4Cl_2$.	$o\text{-}C_7H_7\cdot NO_2$.		$C_2H_4Cl_2$.	$o\text{-}C_7H_7\cdot NO_2$.	
581·5	1493·75	25·994	580·5	1489·5	25·988
582·25	1489·75	25·926	580·75	1490	25·997
582·45	1491·85	25·962	581	1490·35	26·003
582·5	1487·7	25·890	581	1488·25	25·967
582·5	1487·25	25·882	580·1	1492·1	26·034
582·15	1487·45	25·886	580·5	1492·25	26·036
	1487·1	25·880		1490·1	26·000
	1490·7	25·941		1488·05	25·964
	1487·9	25·893		1488·6	25·973
	1491·5	25·956			
	1492·75	25·977			
Means 582·16		25·926	580·64		25·996

Correction : 0·140 for condenser 12 and 0·070 for condenser 13. Whence the true dielectric constant of o-nitrotoluene is 26·066 ± 0·005.

TABLE VIII.

Dielectric Constant of Nitrobenzene.

Condenser No. 14.			Condenser No. 15.		
Capacity.		Apparent D.C.	Capacity.		Apparent D.C.
$o\text{-}C_7H_7\cdot NO_2$.	$C_6H_5\cdot NO_2$		$o\text{-}C_7H_7\cdot NO_2$.	$C_6H_5\cdot NO_2$.	
987·4	1289·8	34·101	976·1	1280	34·092
988·75	1284·6	33·956	979	1277·9	34·037
988·25	1289	34·072	978·25	1278·25	34·046
987	1286·6	34·008	978·25	1279·65	34·083
985	1285	33·966	979·6	1278·65	34·057
984·45	1286·75	34·012	980·6	1278	34·039
983·7	1286·85	34·016			
984·3	1286·8	34·014			
984·45					
985·25					
988					
986·8					
Means 986·1		34·018	978·63		34·059

Correction : 0·082 for condenser 14 and 0·041 for condenser 15. Whence the true dielectric constant of nitrobenzene is 34·093 ± 0·007.

Comparison of the Results.

In order to facilitate the comparison of the foregoing results with those of other investigations, the following tables, based chiefly on recent work, are given.

Benzene.

D.C.	Temp.	Observer.	Method and frequency.
2·288	18°	Turner.[1]	Bridge—telephonic.
2·278	25	Grützmacher.[2]	Valve—radio.
2·27	17	Veley.[3]	Bridge—telephonic.
2·29	10	Errera.[4]	Bridge—radio.
2·268	25	Isnardi.[5]	Resonance—radio.
2·25	—	Klein.[6]	Resonance—radio.
2·268	25	Graffunder.[7]	Valve—radio.
2·24	16	Philip.[8]	Bridge—telephonic.
2·28	—	King and Patrick.[9]	Bridge—telephonic.
2·2402	25·5	Sayce and Briscoe.[15]	Resonance—radio.
2·2482	25	This work.	Bridge—telephonic.

Carbon Tetrachloride.

2·049	12·5°	Veley.[3]	Bridge—telephonic.
2·1831	25	Grützmacher.[2]	Valve—radio.
2·246	18	Turner.[1]	Bridge—telephonic.
2·314	25	Isnardi.[5]	Resonance—radio.
2·219	25	This work.	Bridge—telephonic.

Chloroform.

5·06	—	Joachim.[10]	Bridge—radio.
4·962	25°	Grützmacher.[2]	Valve—radio.
4·811	25	Tangl.[11]	Bridge—telephonic.
5·2	18	Turner.[1]	Bridge—telephonic.
4·760	25	Isnardi.[5]	Resonance—radio.
4·92	—	Klein.[6]	Resonance—radio.
4·93	18	Philip.[8]	Bridge—telephonic.
4·6417	25	This work.	Bridge—telephonic.

Ethylene Dichloride.

10·95	—	Joachim.[10]	Bridge—radio.
10·88	18°	Turner.[1]	Bridge—telephonic.
10·131	25	This work.	Bridge—telephonic.

o-Nitrotoluene.

26·58	15°	Thwing.[12]	Resonance—ultra radio.
27·71	18	Turner.[1]	Bridge—telephonic.
20·3	18	Mathews.[13]	Drude's—ultra radio.
26·066	25	This work.	Bridge—telephonic

Nitrobenzene.

32·19	15°	Thwing.[12]	Resonance—ultra radio.
36·41	18	Turner.[1]	Bridge—telephonic.
34·37	25	Jezewski.[14]	Resonance—radio.
35·57	10	Errera.[4]	Bridge—radio.
36·45		Joachim.[10]	Bridge—radio.
37·1	16	Philip.[8]	Bridge—telephonic.
34·093	25	This work.	Bridge—telephonic.

[1] *Z. physikal. Chem.*, 1900, **35**, 385.　[2] *Z. Physik.*, 1924, **28**, 342.　[3] *Phil. Mag.*, 1906, **11**, 73.　[4] *J. Phys. Radium*, 1922, **3**, 401.　[5] *Z. Physik.*, 1922, **9**, 153.　[6] *Medd. K. Vetenskapsakad. Nobel Inst.*, 1918, **3**, No. 24.　[7] *Ann. Phys.*, 1923, **70**, 225.　[8] *Z. physikal. Chem.*, 1897, **24**, 18.　[9] *J. Amer. Chem. Soc.*, 1921, **43**, 1835.　[10] *Ann. Phys.*, 1919, **60**, 570.　[11] *Ibid.*, 1903, **10**, 748.　[12] *Z. physikal. Chem.*, 1894, **14**, 286.　[13] *J. Physical Chem.*, 1905, **9**, 641.　[14] *J. Phys. Radium*, 1922, **3**, 293.　[15] This vol., p. 315.

Summary.

1. Alternating current bridge methods of determining the dielectric constants of liquids have been discussed critically and experimentally.

2. The method of Nernst and Turner has been criticised.

3. The dielectric constants of specially purified materials have been determined with an accuracy which the author claims has not been previously attained.

CXLVIII.—*A Solid Antimony Hydride.*

By EDWARD JOSEPH WEEKS and JOHN GERALD FREDERICK DRUCE.

THE object of this research was the preparation of a solid antimony hydride,* Sb_2H_2, analogous to Janovsky's solid arsenic hydride (*Ber.,* 1874, **6,** 216; see also Weeks and Druce, *Chem. News,* 1924, **129,** 31, where references to other and more satisfactory methods for its preparation are given).

Sand, Weeks, and Worrell (J., 1923, **123,** 456) showed that the amounts of stibine formed at an antimony cathode during the electrolysis of solutions of sulphuric acid and of sodium hydroxide were definitely related to the temperature and concentration of the electrolyte. In calculating the yields of stibine from the alkaline electrolyte, however, smooth curves could be obtained only

---

* The names "arsenic dihydride" and "antimony dihydride" are suggested, in default of better, for the substances As_2H_2 and Sb_2H_2. The difficulty of nomenclature is increased by the fact that Moser and Brukl (*Monatsh.,* 1924, **45,** 25) state that they have obtained another solid arsenic hydride, As_4H_2, by passing arsine into a hydrochloric acid solution of stannic chloride :

$$5SnCl_4 + 4AsH_3 = As_4H_2 + 5SnCl_2 + 10HCl.$$
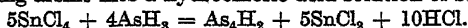
That statement has been confirmed, but whilst their product was amorphous, ours was distinctly crystalline.

Their method was not applicable to the preparation of solid antimony hydride.

by adding together the amount of stibine evolved (calculated from the amount of silver nitrate with which it interacted) and the amount corresponding to the " antimony " deposited in the sodium hydroxide solution. This amorphous deposit of " antimony " was therefore most probably formed by the action of the alkali upon the stibine. Since one of us (E. J. W.) had already observed that the solid deposited in the porous pot during the electrolysis of alkaline solutions at an arsenic cathode was arsenic dihydride, As_2H_2, the deposit of " antimony " was examined; it contained hydrogen and approximately 99% of antimony and proved to be antimony dihydride.

Reckleben and Scheiber prepared arsenic dihydride by the interaction (Z. anorg. Chem., 1911, 70, 255) of arsine with sodium hydroxide and decomposition of the resulting sodium arsenide with water. In consequence of this observation, which we have confirmed, and on the assumption that an atmosphere of hydrogen would favour the formation of antimony dihydride, mixtures of stibine with an excess of purified hydrogen were passed through solutions of sodium hydroxide of various strengths. Solutions stronger than $5N$ gave the desired compound, but the yields were always poor. The reactions which take place may be expressed thus :

$$SbH_3 + 3NaOH = Na_3Sb + 3H_2O.$$
$$2Na_3Sb + 6H_2O = 6NaOH + Sb_2H_2 + 2H_2.$$
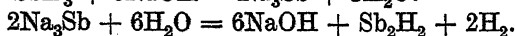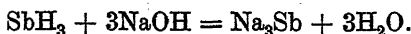
Negative results were obtained when potassium hydroxide was used. Stibine was then passed over solid sodium hydroxide, which soon became coated with a grey deposit. This was decomposed with water, hydrogen being given off, and the residue, after treatment with dilute hydrochloric acid, washing, and drying over calcium chloride in a vacuum desiccator, was antimony dihydride.

The stibine used in these experiments was prepared by dropping a solution of antimony chloride in concentrated hydrochloric acid diluted with its own volume of water into a flask containing zinc and dilute hydrochloric acid. At the end of the experiment, the flask contained a quantity of grey residue, which was insoluble in dilute or concentrated hydrochloric acid. The hydrogen evolved from the zinc and acid, therefore, did not convert all (or even most) of the antimony into stibine; apparently the conditions favoured the formation of a lower hydride :

$$2SbCl_3 + 8H \longrightarrow Sb_2H_2 + 6HCl.$$
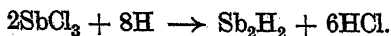
The compound contained a faint trace of iron,* but no zinc,

* This was also detected in the antimony chloride used; the zinc appeared to be free from iron.

carbon, or chlorine.   It contained hydrogen, which it lost on heating
in a vacuum, and which was converted into water when the substance
was ignited in air or oxygen.   A sample which had been kept over
sulphuric acid in a vacuum desiccator for 14 days was heated in a
vacuum, and the hydrogen evolved was measured and the residual
antimony weighed :   0·6566 g. gave 29 c.c. of H_2, measured at
N.T.P., and 0·6506 g. of Sb ; H, 0·40 ; Sb, 99·14.   0·4720 g. gave
0·0357 g. of H_2O ; H, 0·86.   0·4941 g. gave 0·6185 g. of Sb_2O_4 ;
Sb, 98·85 (Sb_2H_2 requires Sb, 99·17 ; H, 0·83%).

Amorphous antimony dihydride dissolved in fairly strong
nitric acid, but was insoluble in other dilute mineral acids and
in concentrated hydrochloric or sulphuric acid.   Concentrated
nitric acid and dilute aqua regia (the most suitable dissolvent)
readily attacked it.   It was insoluble in solutions of the caustic
alkalis.

When heated to dull redness in a current of hydrogen for $\frac{1}{2}$ hour,
the dihydride decomposed slightly, since a little elementary antimony
was deposited on the cooler parts of the tube and a small amount
of silver antimonide (indicating the formation of stibine) was
produced when the escaping gas was passed through silver nitrate
solution.

When the dihydride was heated sufficiently, it became incan-
descent, and then continued to glow until it was converted into a
shining, brittle mass of elementary antimony.   (Arsenic dihydride
exhibits the same phenomenon, but not so strikingly.)

Since we have obtained antimony dihydride by the electrolysis
of sodium hydroxide at an antimony cathode, our compound cannot
be a variety of the well-known "explosive antimony" (Gore,
Phil. Mag., 1855, [iv], 9, 73 ; J., 1863, 16, 365 ; see also Cohen and
Strengers, Z. physikal. Chem., 1904, 50, 291), which contains from
4·8 to 7·9% of antimony trichloride and, according to Pfeiffer
(Annalen, 1881, 209, 161), traces of hydrochloric acid.

Evidence that our product is neither an allotropic variety nor
impure antimony was supplied by dilatometer experiments.   Cohen
and Bosch (Proc. K. Akad. Wetensch. Amsterdam, 1914, 17, 645),
in studying dilatometrically the allotropes of antimony, observed
a transition point at 101°.   When antimony dihydride was
gradually heated with xylene in a dilatometer from 15° to 112°, no
sharp change was observed at 101° or any other temperature.

The dihydride reacted vigorously with fused potassium nitrate,
whilst with powdered (reduced) antimony no such action was
observed, dissolution of the metal in the nitre taking place very
slowly.   The product left after heating the dihydride in a vacuum
behaved like the reduced antimony in this respect.

The authors desire to thank the Research Fund Committee of the Chemical Society for a grant to one of them (J. G. F. D.) which has partly defrayed the expenses of this investigation.

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      ST. JOHN'S HILL, S.W. 11.   [*Received, March 13th*, 1925.]

CXLIX.—*Ring-chain Tautomerism.   Part XIV.   The Structure of Balbiano's Acid.*

By EUGENE ROTHSTEIN, ARNOLD STEVENSON, and JOCELYN FIELD
THORPE.

THE acid $C_8H_{12}O_5$, which Balbiano obtained from camphoric acid and to which he assigned the structure (I), has already been mentioned in Parts I and VII of this series (J., 1922, **121**, 650; 1923, **123**, 2852), and in the latter (Pandya and Thorpe) it was shown that the evidence led to a structure for this acid which represented it, in solution or in the liquid state, as an equilibrium mixture of the two tautomeric individuals (II) and (III), but that in all probability the solid substance melting at 120° was the hydroxy-ring form (III).
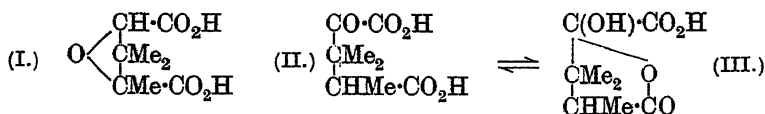
Nevertheless, there were many points which remained ambiguous, especially those in connexion with the arguments Balbiano brought forward in support of his formula, which have hitherto been regarded as conclusive.

In order to make the position clear, it is necessary briefly to recount some of the more salient facts in the history of this acid, which is one that has played such an important part in the determination of the structure of camphor.

Balbiano prepared it by the slow oxidation of camphoric acid (IV) and, in the light of his final decision regarding its structure (I), considered that its formation took place in accordance with the scheme :
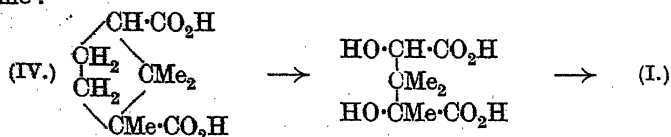
In the course of his experiments, Balbiano reduced the acid (I) to a lactonic acid, $C_8H_{12}O_4$, melting at 163°, to which he gave the

formula (V), and ultimately to αββ-trimethylglutaric acid (VI), the structure of which was proved by the synthesis of Perkin and one of us (J., 1899, **75**, 61). Balbiano was also able to oxidise

$$
\text{(I.)} \quad \overset{\text{H}_2}{\underset{\text{O}}{\rightleftharpoons}} \quad
\begin{array}{l} \text{CH·CO}_2\text{H} \\ | \\ \text{CMe}_2 \quad \text{O} \\ | \\ \text{CHMe·CO} \end{array}
\quad \text{(V.)} \quad \overset{\text{H}_2}{\rightarrow} \quad
\begin{array}{l} \text{CH}_2\text{·CO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{CHMe·CO}_2\text{H} \end{array}
\quad \text{(VI.)}
$$
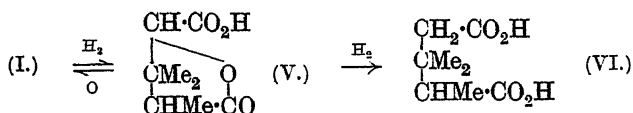
his lactonic acid (V) back to the original acid (I) by means of permanganate.

Blanc (*Bull. Soc. chim.*, 1901, **25**, 68), in his attempt to synthesise Balbiano's acid, prepared a lactonic acid melting at 163° isomeric with the lactonic acid (V), but which he found to be unaltered by permanganate. Blanc's lactonic acid was prepared from dimethyllævulic acid (VII) through the addition of hydrocyanic acid and hydrolysis and, therefore, could only have the structure (VIII). The discovery of this compound led Balbiano to re-examine the lactonic acid he had prepared by the reduction of his acid (I), with

$$
\text{(VII.)} \quad
\begin{array}{l} \text{CH}_2\text{·CO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{MeCO} \end{array}
\quad \rightarrow \quad
\begin{array}{l} \text{CH}_2\text{·CO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{MeC(OH)·CN} \end{array}
\quad \rightarrow \quad
\begin{array}{l} \text{CH}_2\text{—CO} \\ | \quad\quad | \\ \text{CMe}_2 \quad \text{O} \\ | \\ \text{CMe·CO}_2\text{H} \end{array}
\quad \text{(VIII.)}
$$
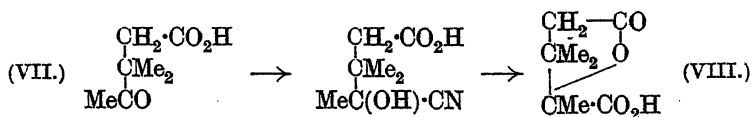
the result that he was able to isolate, by means of the barium salts, two lactonic acids, one melting at 163° and the other at 165°.

The outcome is remarkable, because whilst Blanc states (*loc. cit.*) that Balbiano's lactonic acid depressed the melting point of his lactonic acid to about 115°, Balbiano asserts that this figure is incorrect (*Centr.*, 1902, II, 573), for in his hands the mixture of the lactonic acids prepared by him melted only 5° lower. Balbiano's conclusion is that by the reduction of his acid (I) he had prepared both the lactonic acids (V) and (VIII) and it is this proof which he, quite rightly, regarded as decisive, since it is only possible to obtain these substances from his "oxide" formula, and any other expressions, such as, for example, the ketone formula of Mahla and Tiemann become untenable.

$$
\text{(V.)} \quad \leftarrow \quad
\begin{array}{l} \text{CH(OH)·CO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{CHMe·CO}_2\text{H} \end{array}
\quad \overset{\text{H}_2}{\leftarrow} \quad \text{(I.)} \quad \overset{\text{H}_2}{\rightarrow} \quad
\begin{array}{l} \text{CH}_2\text{·CO}_2\text{H} \\ | \\ \text{CMe}_2 \\ | \\ \text{C(OH)Me·CO}_2\text{H} \end{array}
\quad \rightarrow \quad \text{(VIII.)}
$$
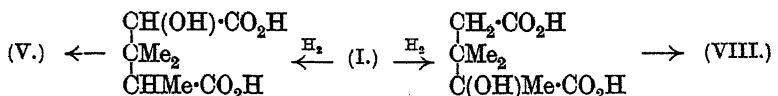
Here the matter rested until 1923, when Pandya and one of us (*loc. cit.*) isolated both Blanc's lactonic acid (m. p. 165·5°) and Balbiano's lactonic acid (m. p. 163°) from the products obtained by the monobromination of αββ-trimethylglutaric acid, and it was then

that the first doubts as to the correctness of Balbiano's observations arose, because Blanc's statement that the mixture of the two substances melted at about 115° was confirmed (loc. cit., p. 2863). It was clear, therefore, that Balbiano could not have used Blanc's lactonic acid in the experiment he describes.

The two lactonic acids prepared by Pandya and Thorpe were obtained in very different proportions, the higher-melting compound largely predominating.   It was clear that they were derived from the only two monobromo-derivatives possible, namely, (IX) and (X),

$$
\begin{array}{ll}
& \text{CH}_2\text{·CO}_2\text{H} \qquad\qquad\quad \text{CHBr·CO}_2\text{H} \\
(\text{IX.}) \quad & \text{CMe}_2 \qquad\qquad\qquad\quad\ \text{CMe}_2 \qquad\quad (\text{X.}) \\
& \text{CBrMe·CO}_2\text{H} \qquad\qquad \text{CHMe·CO}_2\text{H}
\end{array}
$$

but there was no evidence to show which was which. The higher-melting compound was, however, clearly identical with that prepared by Balbiano by a very similar method and to which he assigned the structure (V), although he did so merely on the ground that bromination of αββ-trimethylglutaric anhydride would *probably* lead to the bromo-acid (X).   In the same paper, he stated that the compound was also obtained by the reduction of the acid, m. p. 120°, although he does not mention having made a direct comparison of the two products (*Rend. Accad. Lincei*, 1899, 8, 422).

A review of the whole subject showed the existence of many ambiguities and contradictions, which could only be removed in a satisfactory manner by preparing Blanc's lactonic acid (VIII) and carrying out a series of direct comparisons.   At the time this difficult preparation could not be accomplished, but it has now been carried out and the chemistry of this important chapter in the history of the structure of camphor is, at last, quite clear.   The position may be summarised as follows :

(1) The lactonic acids prepared by Balbiano by the reduction of the acid, m. p. 120°, are not identical with Blanc's synthetic lactonic acid.   We have carefully repeated the reduction and have isolated a lactonic acid, m. p. 162—163°, which depressed the melting point of the synthetic acid some 40° in accordance with Blanc's observation.   The lactonic acid, m. p. 162—163°, was the sole product of the reaction; we have made repeated attempts to resolve it into two components as described by Balbiano (*loc. cit.*), but without success.   It may be mentioned that an acid of the formula (V) can exist in two stereoisomeric modifications, of which the compound, m. p. 162—163°, prepared by Balbiano and by ourselves must be one.   Balbiano's observation that the alleged mixture of the two compounds (in the ratio 2 : 1) originally obtained melts at 163°, whilst a mixture of equal parts of his two pure isomerides melts

at 158° is clearly unsatisfactory, but it proves quite definitely that the second substance, if any, present in the original mixture cannot have been Blanc's lactonic acid. Mixtures of this acid with the acid, m. p. 162—163°, in widely different proportions melt very much lower, as already mentioned.

(2) Blanc's lactonic acid has the formula (VIII) and can exist only in one inactive modification. As already stated, it is not produced by the reduction of Balbiano's acid, but is, however, the chief product formed in the monobromination of αββ-trimethyl-glutaric acid.

As regards the melting point of Blanc's lactonic acid, it is clear that the figure given by Blanc is too low and should have been 165·5°.

(3) The lactonic acid melting at 165·5—166° described by Pandya and Thorpe has the formula (VIII) and not the formula (V), and that melting at 163° has the formula (V) and not the formula (VIII). The descriptions of these substances must therefore be interchanged in the reference cited. It is unfortunate, but was in the circumstances inevitable, that the lactonic acid melting at 163° should have been used for the purpose of identifying the lactonic acid prepared by Chandrasena, Ingold, and Thorpe (J., 1922, 121, 1550) from α-campholytic acid on oxidation, and that the identity of the two should have been advanced by them as proof of the existence of a bridged phase in α-campholytic acid. It is now clear that the lactonic acid prepared by these investigators has the formula (VIII) and that the supposed " proof " is without significance.

It follows, therefore, that Balbiano's " oxide " formula for the acid $C_8H_{12}O_5$ is incorrect and that the evidence brought forward in Parts I and VII of this series, which need not be recapitulated here, shows conclusively that this substance exhibits keto-cyclol tautomerism of the kind suggested. In order, however, still further to confirm this and, incidentally, to ascertain if other compounds, similar in structure to the lactonic acid (V), also exist in stereo-isomeric forms which also possess similar melting points and show no mutual depression of the melting point when mixed, we have carried out a series of comparative experiments between Balbiano's acid (I) and the next lower homologue.

It is a curious fact that this substance was prepared, and its properties studied, many years ago by Perkin and one of us (J., 1901, 79, 729) and was isolated only in the hydrated form (XI), but we now find that it can readily be converted into the diethyl ester and that this does not contain water of hydration. It must therefore have the structure (XII). Balbiano's acid also can be easily converted into the diethyl ester and since, in this compound,

there is no possibility of the occurrence of tautomerism, it must have the structure (XIII). The two esters, therefore, are directly

$$
\begin{array}{lll}
\text{C(OH)}_2\text{·CO}_2\text{H} & \text{CO·CO}_2\text{Et} & \text{CO·CO}_2\text{Et} \\
\text{(XI.)} \quad \text{CMe}_2 & \text{(XII.)} \quad \text{CMe}_2 & \text{CMe}_2 \qquad \text{(XIII.)} \\
\text{CH}_2\text{·CO}_2\text{H} & \text{CH}_2\text{·CO}_2\text{Et} & \text{CHMe·CO}_2\text{Et}
\end{array}
$$
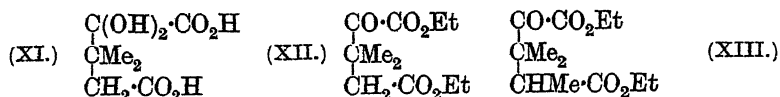
comparable and should, if our hypothesis is correct, serve as bases for the comparative experiments we have outlined.

It will be noticed that if the keto-ester (XII) is treated with ethyl bromoacetate and zinc (the usual Reformatski reaction), it should be converted into a hydroxy-tribasic ester (XIV) which should lose ethyl alcohol on distillation and yield the lactone of a dibasic ester (XV), which can exist in only one inactive modification.

$$
\begin{array}{ll}
\text{CO}_2\text{Et·CH}_2\text{·C(OH)·CO}_2\text{Et} & \text{CO}_2\text{Et·CH}_2\text{·C·CO}_2\text{Et} \\
\text{(XIV.)} \qquad \text{CMe}_2 & \qquad\qquad\qquad\quad \text{CMe}_2\ \ \text{O} \quad \text{(XV.)} \\
\qquad\qquad \text{CH}_2\text{·CO}_2\text{Et} & \qquad\qquad\qquad\quad \text{CH}_2\text{—CO}
\end{array}
$$

(One inactive form.)
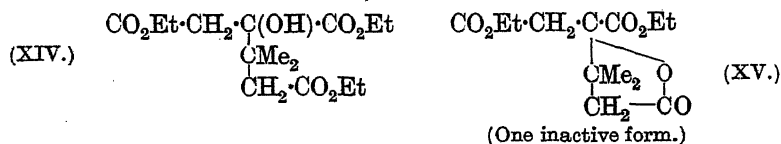
On the other hand, if the ester (XIII) were treated in a similar manner, the lactonic dibasic ester (XVII) which will be formed from the hydroxy-tribasic ester (XVI) on distillation will be capable of existence in two inactive modifications. Experiment shows this

$$
\begin{array}{ll}
\text{CO}_2\text{Et·CH}_2\text{·C(OH)·CO}_2\text{Et} & \text{CO}_2\text{Et·CH}_2\text{·C·CO}_2\text{Et} \\
\text{(XVI.)} \qquad \text{CMe}_2 & \qquad\qquad\qquad\qquad\quad \text{(XVII.)} \\
\qquad\qquad \text{CHMe·CO}_2\text{Et} & \qquad\qquad\qquad \text{CMe}_2\ \ \text{O} \\
& \qquad\qquad\qquad \text{CHMe·CO}
\end{array}
$$

(Two inactive forms.)
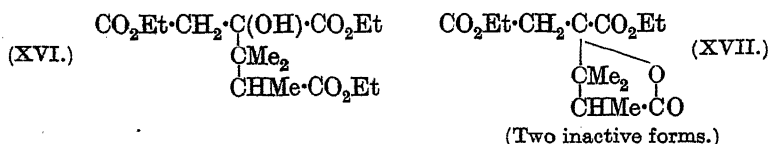
to be the case. The lactonic dibasic ester (XV) is obtained in one well-defined form, and the lactonic ester (XVII) in two distinct stereoisomeric modifications, m. p. 86° and 115°, respectively. These two substances cause a considerable depression in the melting point when mixed, and this observation further strengthens our belief that Balbiano could not have isolated the two stereoisomerides of the lactonic acid (V) predicted by theory.

On hydrolysis, both the stereoisomeric esters give the same lactonic acid, m. p. 178° (XVIII), whilst a second isomeric acid, m. p. 140°, is isolated from the higher-melting ester. The acids, m. p.'s 178° and 140°, are doubtless stereoisomerides like the ester, the lower-melting lactone probably having the *cis*-structure, as it decomposes at the melting point; the product is probably an an-hydride analogous to (XIX) described below.

The ester (XV) can be hydrolysed in the same way to the corre-sponding lactonic acid, which passes very readily to the anhydride

(XIX); in fact the change takes place on keeping the acid, so that the two are generally obtained together.

(XVIII.) $CO_2H \cdot CH_2 \cdot C \cdot CO_2H$ / CMe_2 O / $CHMe \cdot CO$

CO————O / $CH_2 \cdot C$————CO / CMe_2 O / CH_2——CO (XIX.)
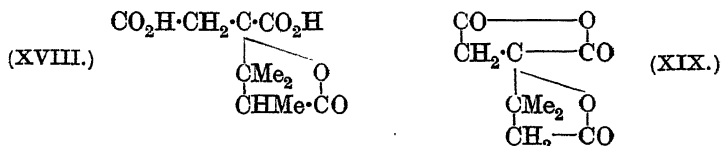
It is perhaps interesting to note, especially in view of the different opinions which are held regarding the intervention or non-intervention of water in the mutarotation of sugars, that when the molecular conditions are present, as is the case in Balbiano's acid, which lead to tautomeric change in solution or in the liquid state, the substance shows no tendency to exist in the hydrated form. If, however, as in the next lower homologue, these conditions are absent, the ketone exists in the hydrated state and only passes into the anhydrous condition when the water is driven off by heat. The fact, therefore, that the mutarotatory sugars are not hydrated is significant.

EXPERIMENTAL.

α-Keto-ββ-dimethylpentane-αγ-dicarboxylic Acid (Balbiano's Acid).—Balbiano's directions for preparing the acid (*Rend. Accad. Lincei*, 1892, **1**, 278; *Ber.*, 1894, **27**, 2133) were followed, but, as at the ordinary temperature decoloration of the permanganate took some months, the oxidation was carried out at 28—30°, when it was completed in from 4 to 6 weeks. The yield from 450 g. of camphoric acid was about 80 g. of the calcium salt, from which about 45 g. of the acid were obtained. Previous investigators were unable to recrystallise the acid, but from a very concentrated solution in chloroform it separates in stellate clusters of prisms [Found: C, 51·0; H, 6·4; *M* (dibasic), 92. Calc., C, 51·0; H, 6·4%; *M*, 94].

The *diethyl* ester (XIII), a slightly viscous liquid, b. p. 148—149°/ 11·5 mm., is best prepared by Phelp and Tillotson's alcohol vapour method (yield 75%), as the ordinary methods give very poor results (Found: C, 58·4; H, 8·25. $C_{12}H_{22}O_5$ requires C, 59·0; H, 8·3%).

γ-Lactone of α'-Hydroxy-αββ-trimethylglutaric Acid (V).—A mixture of Balbiano's acid (12 g.), hydriodic acid (d 1·7; 40 c.c.), and red phosphorus (4 g.) was heated under reflux for 5 hours, diluted with water, the excess phosphorus filtered off, and the filtrate extracted with ether. The ethereal extract was successively washed with water, sodium thiosulphate, and again with water, and the ether removed. The residue was dissolved in water, neutralised with sodium hydroxide, and boiled with calcium chloride (30%), when calcium trimethylglutarate was precipitated (Balbiano, *loc. cit.*).

The filtrate was acidified with hydrochloric acid and extracted with ether; the extract on evaporation gave a solid which on crystallisation from ethyl acetate and light petroleum (b. p. 40—60°) melted at 163° (Found : C, 55·6; H, 7·1. Calc., C, 55·8; H, 7·0%). Repeating Balbiano's work, the barium salt of this lactonic acid was fractionally crystallised and the acids were regenerated from the two fractions, but it was found that the melting points were 162—163° and 163—164°, respectively, and that there was no depression of the m. p. when the two were mixed.

γ-*Lactone of* α-*Hydroxy*-αββ-*trimethylglutaric Acid* (*Blanc's Lactone*) (VIII).—ββ-Dimethylsuccinic acid, prepared from acetone cyanohydrin and ethyl cyanoacetate (Higson and Thorpe, J., 1906, 89, 1465), was heated under reflux with acetyl chloride to form the anhydride (b. p. 110°/16 mm.), and from this the chloride of α-carbethoxy-β-methylpropane-β-carboxylic acid, $CO_2Et·CH_2·CMe_2·COCl$, was obtained as described by Blaise (*Compt. rend.*, 1899, 128, 183). Instead of converting this into ethyl ββ-dimethyl-lævulate with zinc methyl, it was found more convenient to employ the Blaise-Maire method (compare Birch, Kon, and Norris, J., 1923, 123, 1370) (yield 78%). The acid obtained by the hydrolysis of this ester was treated with potassium cyanide, and the resulting nitrile hydrolysed as described by Blanc (*loc. cit.*); the lactonic acid separated from water in needles, m. p. 165·5° (Found : C, 55·9; H, 7·25. Calc., C, 55·8; H, 7·0%). The m. p. of the mixture with the γ-lactone of α′-hydroxy-αββ-trimethylglutaric acid was 116—117°.

γ-*Lactone of* δε-*Dicarbethoxy*-δ-*hydroxy*-γγ-*dimethylpentane*-β-*carboxylic Acid* (XVII).—A mixture of ethyl α-keto-ββ-dimethylpentane-αγ-dicarboxylate (24·4 g.), ethyl bromoacetate (11·1 c.c.), benzene (50 c.c.), and zinc wire (6·5 g.) was heated under reflux on the steam-bath. Reaction only took place when a crystal of iodine was added and required 3—4 hours for completion. It can be accelerated by adding a small quantity of magnesium filings, but the yield is considerably reduced thereby. The product was isolated in the usual manner and distilled, when the main portion, b. p. 180—220°/20 mm. (yield 6—7 g.), solidified on cooling. The solid was crystallised from light petroleum (b. p. 40—60°), to which a few drops of benzene were added, and gave two distinct types of crystals which were separated by hand. On recrystallisation from the same solvent, these gave, respectively, needles, m. p. 86° (Found : C, 58·6; H, 7·8. $C_{14}H_{22}O_9$ requires C, 58·7; H, 7·8%), and minute prisms, m. p. 115° (Found : C, 58·7; H, 7·9). The m. p. of the mixture was 75°. It was subsequently found that a better separation was obtained by dissolving the crude substance in dilute alcohol, from which the lactone, m. p. 115°, separates more readily.

Products of hydrolysis. The lactone, m. p. 115° (2·5 g.) was heated under reflux for 5 hours with 50% aqueous potassium hydroxide (50 c.c.). The resulting solution was acidified and extracted with ether, the ethereal extract yielding a solid, which effervesced on treatment with sodium hydrogen carbonate and, after crystallisation from ethyl acetate and light petroleum (b. p. 40—60°), melted at 140° *with* decomposition (Found : C, 51·5; H, 6·2. $C_{10}H_{14}O_6$ requires C, 52·2; H, 6·1%). On keeping the mother-liquor, a second acid separated melting at 178° *without* decomposition (Found : C, 52·7; H, 6·3%). A mixture of the two acids melted at 122—125°.

The lactone, m. p. 86°, on similar treatment yielded a product which on crystallisation from ethyl acetate and light petroleum (b. p. 40—60°) melted at 122—125° and was probably a mixture of the two acids described above. None of the acid, m. p. 140°, could be isolated, as repeated crystallisation only gave acid, m. p. 178°, which was identical with that described above. If the esters are hydrolysed with hydrochloric acid (10%) instead of with potassium hydroxide, only 1 mol. of alcohol is eliminated. The lactone, m. p. 86°, gives an acid which after crystallisation from benzene and light petroleum has m. p. 146° (Found : C, 55·9; H, 7·25. $C_{12}H_{18}O_6$ requires C, 55·8; H, 7·0%); that from the lactone, m. p. 115°, crystallised from the same solvent, has m. p. 123° (decomp.) (Found : C, 56·4; H, 7·2%). When mixed, the two acids melted at 113°.

Ethyl α-keto-ββ-diethylglutarate * (XII) was obtained by a modification of Singh and Thorpe's method (J., 1923, **123**, 120) for the preparation of the corresponding methyl-ethyl acid.

Ethyl Methoxycaronate, $Me_2C{<}{C(OMe)·CO_2Et \atop CH·CO_2Et}$.—Ethyl αα'-di-bromo-ββ-dimethylglutarate (150 g.) was slowly added to 20 g. of sodium in 300 c.c. of methyl alcohol, and the mixture heated under reflux for 5 hours. The excess of alcohol was evaporated and the residue dissolved in water, acidified with dilute hydrochloric acid, and extracted with ether. The ethereal extract, after washing with dilute sodium carbonate, gave an oil, b. p. 120°/18 mm. (Found : C, 58·5; H, 7·5. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·1%).

α-Keto-ββ-dimethylglutaric Acid.—Ethyl methoxycaronate (70 g.) (or the acid) and hydrobromic acid (*d* 1·5; 500 c.c.) were gently heated on a sand-bath, special caution being observed in the case of the ester, and finally boiled for 2 hours. On evaporation, a dark coloured solid remained, which was the acid in its hydrated form, m. p. 84° (yield nearly theoretical).

The acid was esterified with alcohol and sulphuric acid, the ester

* For this and the following experiments, we are indebted to Dr. B. Singh.

boiling at 140—141°/13 mm. (Found : C, 58·0; H, 8·1. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·8%).

Lactone of γδ-Dicarbethoxy-γ-hydroxy-ββ-dimethylbutane-α-carboxylic Acid (XV).—The keto-ester was treated with ethyl bromoacetate and zinc as described above, the operation requiring 7—8 hours for completion.   The product on distillation yielded a thick oil, b. p. 198—204°/9 mm. (Found : C, 56·8; H, 7·6. $C_{13}H_{20}O_6$ requires C, 57·3; H, 7·3%), which on keeping formed a crystalline mass, m. p. 54°.

Products of hydrolysis.   The ester (36 g.) was boiled for 3 hours with sodium hydroxide (36 g.) in 145 c.c. of water and 230 c.c. of alcohol, the alcohol being then evaporated off.   Water was added and the acidified liquid extracted with ether, the ethereal extract yielding on evaporation a mixture of two substances which were readily separated by treatment with ether.   The insoluble portion is the acid corresponding to the lactone, m. p. 54°.   It melts at 132° (decomp.) [Found : C, 49·9; H, 5·5. $C_9H_{12}O_6$ requires C, 50·0; H, 5·6%.   Silver salt : Found, Ag, 58·1.   Calc. (tribasic), Ag, 58·3%].   The soluble portion is evidently the anhydride of the above acid (XIX).   Crystallised from benzene, it formed shining needles, m. p. 126—128° (Found : C, 54·3; H, 5·0. $C_9H_{10}O_5$ requires C, 54·5; H, 5·0%).   It is also formed when the acid is kept for some days.

We are indebted to the Chemical Society for a grant which has partly defrayed the cost of the materials required for the investigation.

CL.—*Studies of Dynamic Isomerism.   Part XVII. The Mutarotation of Aluminium Benzoylcamphor.*

By IRVINE JOHN FAULKNER and THOMAS MARTIN LOWRY.

THE preceding paper of this series (J., 1924, **125**, 2081) described the discovery in beryllium benzoylcamphor * of a new type of mutarotation, which differs fundamentally from the familiar mutarotation of prototropic compounds in that (i) it occurs in a compound containing no mobile hydrogen atom, and (ii) instead

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* The formula from which the theoretical composition of this compound was calculated was given erroneously as $C_{34}H_{38}O_2Be$ instead of $C_{34}H_{38}O_4Be$ on pp. 2087 and 2088 of this paper.

of being arrested, it is accelerated in a remarkable degree in solutions in chloroform, with which the solute also forms a crystalline addition compound. The mutarotation was therefore attributed to a reversal of sign in an optically active beryllium atom, forming the centre of a fourfold co-ordination complex, in which both chelate groups are themselves optically active. The optical activity of a coloured metal in a complex of this kind can sometimes be detected by means of the Cotton phenomenon, which has been observed in the case of *copper, tervalent cobalt*, and *chromium*, but not in bivalent *nickel* and *cobalt* (Lifschitz, *Z. physikal. Chem.*, 1923, **105**, 27), where the four co-ordination positions may have a square instead of a tetrahedral configuration. In the case of *aluminium*, the absence of visible colour makes this method of detecting the optical activity of the metal impracticable, but enables us to look for it by observations of mutarotation.

Aluminium benzoylcamphor has now been observed to undergo mutarotation in four different solvents. The observed changes represent only a small fraction of the rotatory power of the compound, but they are quite unmistakable, since the total change of about 3° in the actual readings for a solution in benzene corresponds with an alteration of 30° in the specific rotatory power, and of about 200° in the molecular rotatory power of the compound. Mutarotation has also been observed in solutions in ethylene bromide, chloroform, and acetone. The mutarotation in ethylene bromide was very slow, extending over a period of about a week. In acetone and in chloroform, just as in the case of the beryllium compound, the change was rapid, the action being complete in the course of a few minutes, instead of extending over several days. The fact that the mutarotation in chloroform is in the opposite direction to that in benzene, ethylene bromide, or acetone, was confirmed by repeating the observations. It suggests, even if it does not prove, the formation in solution of a chloroform compound of higher rotatory power than the original material. The reversibility of the chemical changes by which the mutarotation is brought about was proved, as in the case of the beryllium compound, by recovering the original material and repeating the mutarotation both in benzene and in chloroform.

The curves showing the mutarotation of beryllium benzoylcamphor in benzene showed a well-marked lag, followed by a progressive speeding up of the action, but nothing of the kind was observed in solutions to which pyridine was added. The lag was therefore obviously due to the fact that *the mutarotation in benzene is not spontaneous*, but depends (like that of nitrocamphor and the sugars) on the intervention of a catalyst, which is gradually picked

up by the solution, e.g., from the vessel in which it is examined. The curves for solutions containing pyridine were, moreover, at least approximately monomolecular in form; and although the velocity coefficients show the usual slight fluctuations, they are sufficiently exact to prove that *the mutarotation of beryllium benzoylcamphor obeys the monomolecular law.* This is no longer true for the solutions now under discussion, since *the velocity of mutarotation of aluminium benzoylcamphor falls off much more rapidly than a monomolecular law would allow.* The data indeed suggest that the mutarotation in benzene is probably governed by a trimolecular law, since the velocity of change is approximately proportional to the *cube* of the concentration, although the trimolecular velocity coefficients vary appreciably during the course of the change. This result may perhaps be associated with the necessity for inverting the points of attachment of *three* chelate groups in order to reverse the optical activity of the aluminium.

EXPERIMENTAL.

Aluminium benzoylcamphor was prepared by the method used by Burgess and Lowry for the preparation of beryllium benzoylcamphor (J., 1924, **125**, 2087). A slight excess of " pure " aluminium sulphate, dissolved in hot water, was added to equivalent quantities of piperidine and of benzoylcamphor dissolved in hot alcohol. The brownish-red precipitate, collected after heating on the water-bath for $\frac{1}{2}$ hour, was washed with hot alcohol and crystallised from chloroform–acetone, a small yield of colourless material being obtained after a large number of recrystallisations. By observing the absorption spectrum, the colour was proved to be due to traces of iron from the aluminium sulphate; by adding successive small portions of benzoylcamphor (with its equivalent of piperidine) to the whole of the aluminium sulphate, however, most of the iron was removed in the first two fractions and the final fraction was almost colourless.

The compound forms microscopic crystals, and all attempts to grow crystals for measurement were unsuccessful; under the microscope these crystals appear as plates, which resemble the chromium compound. After two crystallisations the compound melted at 227—228° (Found : C, 76·8; H, 7·4; Al, 3·5. $C_{51}H_{57}O_6Al$ requires C, 77·2; H, 7·25; Al, 3·4%).

Aluminium benzoylcamphor is insoluble in aqueous solvents, and only slightly soluble in acetone and ethyl acetate; it is deposited as a glass from cold benzene (which dissolves about 5%) and from chloroform (which dissolves about 30%), but can be prepared in a crystalline form by adding two volumes of acetone

to a saturated solution in chloroform or benzene. Crystallisation is complete only after several weeks.

Mutarotation.—On account of its colour and limited solubility, the substance (which had been crystallised from chloroform-acetone and dried in a vacuum for 7 days) was examined in a $2\frac{1}{2}\%$ solution in chloroform or benzene, and in a saturated solution in acetone or ethylene bromide.

FIG. 1.

Mutarotation of aluminium benzoylcamphor.
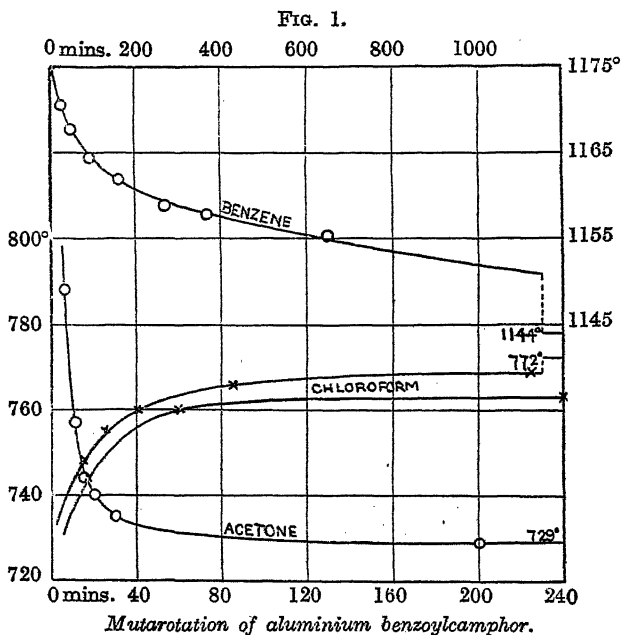
TABLE I.

Mutarotation in Chloroform.

$2\frac{1}{2}\%$ Soln. in 4-dcm. tube at 20°. (a) Time (min.).	$[a]_{5461}$.		$2\frac{1}{2}\%$ Soln. in 2-dcm. tube at 20 (b) Time (min.).	$[a]_{5}$	
0	(730°)		0	(718°)	
15	748	0·037	17	744	0·051
25	755	0·036	60	760	
40	760	0·031	Final	763	
85	766	0·023			
235	769	0·014			
Final	772				

After the mutarotation recorded in Table I*a* was complete, 20 c.c. of the solution were evaporated twice to dryness with chloroform and acetone to give a crystalline product, made up again to 20 c.c. with chloroform, and re-examined in a 2-dcm. tube,

when the data of Table I*b* were recorded. The "velocity co-efficients" (for a monomolecular action) were of the same order of magnitude as before, but the second mutarotation was distinctly faster than the first, probably because the material was less pure.

TABLE II.

Mutarotation in Benzene at 20°

Time (min.).	$[a]_{5461}$.	k_{mono}.	k_{tri}.	Time (min.).	$[a]_{5461}$.
				(b) $2\frac{1}{2}\%$ tube (recovered from II*a*).	
0	(1175·0°)	—	—	0	—
25	1170·5	0·0062	0·000055	30	1156·6°
48	1167·7	0·0055	0·000068	45	1155·6
90	1164·3	0·0047	0·000070	Final	1155·2
160	1161·8	0·0034	0·000062		
265	1158·9	0·0027	0·000062	(c) 2% Soln. in 4-dcm.	
365	1157·8	0·0022	0·000055	tube.	
650 *	1155·3	0·0016	0·000050	0	—
1470 *	1149·5	—	—	20	1175·0
1890	1147·6	—	—	25	1161·5
Final	1143·8	—	—	32	1154·9
				Final	1154·1

* Water-circulation stopped during the night between these two readings.

On recovering the material after the first slow mutarotation in benzene (Table II*a*), only the final indications of a very fast mutarotation (Table II*b*) could be observed. Another solution, prepared from the original material and the same solvent, also gave a mutarotation (Table II*c*) many times faster than in the first experiment, probably on account of catalysis by pyridine, which had recently been much used in the laboratory.

TABLE III.

Mutarotation in Acetone at 20°.

Time (min.)	0	6	11	15	20	30	Final (24 hrs.)
a_{5461}	—	6·75°	6·48°	6·37°	6·34°	6·29°	6·24°
$[a]_{5461}$	—	788	757	744	740	735	729

The solution was prepared by shaking the finely-divided solid with acetone for 5 minutes and then filtering into the tube. The concentration was estimated by evaporating 10 c.c. to dryness and weighing the residue.

The solutions were prepared by shaking 0·4 g. of the salt with about 30 c.c. of solvent and filtering; the concentration of the second solution was determined by evaporation, and that of the first solution was calculated to give the same final specific rotatory power.

In Table IV*a* the water-circulation was maintained during the first 6 hours but not during the subsequent nights; but all readings

TABLE IV.

Mutarotation in Ethylene Bromide.

Saturated soln. in 4-dcm. tube.

(a) [a] = 22·0 a.		(b) [a] = 22·5 a.			
Time (min.).	$[a]_{5461}$.	Time (min.).	$[a]_{5461}$ obs.	$[a]_{5461}$ calc.	Obs. — calc.
		20	583°		
30	570°	23	576		
45	566	25	574		
75	565	30	569	570°	−1°
195	564	45	567	568	−1
360	562	100	564	564	±
1320	558	300	561	556	+5
1860	553	530	557	552	+5
2820	550	1560	547	547	±
4200	546 ·	2100	545	545	±
5640	545	2880	542	544	−2
9 days (final)	538	Final	538	538	±
				Mean k = 0·0000040	

were taken at 20°. Table IV*b* shows that after the first half-hour the course of the curve conforms roughly to a *trimolecular* law.

CLI.—*" Activated " Graphite as a Sorbent of Oxygen.*

By DONALD HUGH BANGHAM and JOHN STAFFORD.

IN the course of an investigation of the disappearance of hydrogen in discharge tubes, it was noticed that the graphite cathode, which had been made to take up relatively large quantities of hydrogen under the influence of the discharge, showed remarkably enhanced activity as a sorbent of ordinary (*i.e.*, molecular) oxygen. This circumstance was not in itself surprising in view of the experiments of Langmuir on atomic hydrogen, in which it was shown that the glass surfaces which had been exposed to hydrogen at low pressures in the presence of hot metallic filaments were capable of taking up measurable quantities of oxygen when the filaments had been allowed to cool and the hydrogen replaced by the latter gas (Langmuir, *J. Amer. Chem. Soc.,* 1912, **34**, 1310). Nevertheless, it seemed worth while to examine in some detail the kinetics of the oxygen disappearance, in order to see whether, and how far, the time-equations governing it would differ from those previously found to hold for cases of sorption of a more usual type.

Investigation showed that the sorption of oxygen, both by the original and by the hydrogen-treated graphite, took place at constant pressure in obedience to an equation of the type

$$s = kt^b,$$

s being the quantity of oxygen sorbed at time t after its introduction to the graphite, and k and b being constants. The sorption is therefore exactly similar in type to that of ammonia, carbon dioxide, nitrous oxide, etc., on glass, the same anomalous time-law holding in these instances (Bangham and Burt, *Proc. Roy. Soc.,* 1924, *A*, **105**, 481).

Experimental.

The graphite used was a sample of the artificial variety supplied by the Acheson Graphite Co. A small glass bulb carrying a short platinum electrode at the bottom was partly filled with the finely-powdered material and sealed at its open end to a stem of quill tubing provided with a second electrode at some 10 cm. from the junction. The open end of the quill was sealed to a wide-bore tap which communicated with a gas-measuring system comprising a McLeod gauge and a calibrated tube containing phosphorus pentoxide. Other taps connected the measuring system through pentoxide tubes with the hydrogen and oxygen trains, and with the pumps. A rapid-acting type of high-vacuum pump was used, backed by a double-fall Sprengel which exhausted the gas to the water-pump. This pumping system was capable of maintaining over the heated graphite, even when it was parting with gas at a detectable rate, a pressure quite unmeasurable by the McLeod gauge.

After the graphite had been thoroughly exhausted in the cold, its temperature was raised to 350° and the pumping continued. Although graphite is usually considered inactive as a sorbent, this treatment caused it to yield considerable quantities of gas, and the rate of evolution became inappreciable only after several hours. The vacuum-heating was normally continued for about 72 hours, but no claim can be made that the graphite was rendered gas-free by this treatment, and there is no doubt that a rise of temperature above 350° would have led to further evolution. The treatment was nevertheless sufficient to secure that on allowing the solid to stand for 24 hours at room temperature no detectable gas developed in the system, whilst even at 350° the further evolution during the same period amounted to only a few cubic millimetres (N.T.P.).

The Disappearance of Hydrogen under the Influence of the Discharge.

The graphite, even after vacuum-heating, showed no tendency to take up measurable quantities of molecular hydrogen. This

fact, which was established by making a water-calibration of the containing bulb, enabled the deadspace volumes of bulbs subsequently used to be determined with hydrogen.

Immediately the discharge was begun the disappearance of the hydrogen was rapid, and it slowed down only when the pressure of the gas had fallen considerably. The particles near the surface of the graphitic cathode were thrown into a state of turbulence, and flashes of white light appeared in the same region. As the discharge continued, the graphite formed a coating on the surface of the tube which crept gradually upwards towards the anode, but fell back in patches and left the glass clear. At low pressures, the creeping of the graphite was more marked, the graphite gradually coating the tube from cathode to anode. Attempts to prevent this creeping by inserting a plug of glass wool in the stem of the tube led invariably to the fracturing of the tube at this point. In the absence of the plug, the tube frequently fractured opposite the upper surface of the graphite, practically all the heat being developed in this region.

If at any time the discharge were cut off, the pressure remained perfectly constant until its renewal.

Undoubtedly a certain amount of electrolysis of the glass took place, and the glass walls may also have contributed to a minute extent to the disappearance of hydrogen. A blank experiment, in which no graphite was used, showed, however, that the pressure changes caused by action at the surfaces of the glass and of the platinum wires amounted only to about 0·2% of those normally experienced.

The General Nature of the Phenomenon.

The following description of a series of typical experiments will serve to illustrate the general nature of the phenomenon. The amount of graphite used was 11 g. In order to render as comparable as possible the tests of its activity towards oxygen and carbon dioxide the gases were invariably introduced at the same pressure (ca. 0·4 mm.). In cases where the activity of the graphite was small, this pressure remained almost constant throughout the experiment; in other cases, it was necessary on occasions to renew the supply of gas in the system to approximate to this condition.

I. After the graphite had been submitted to vacuum-heating for the normal period of 72 hours, its "original" activity towards oxygen was determined. The sorption values at different times are given in Table I (Column A), in juxtaposition to those calculated from the equation $s = 2·9 \times t^{0·190}$.

II. The oxygen was pumped out, and the graphite submitted to

a further 18 hours' vacuum-heating, following which its activity towards oxygen was redetermined. The results appear in column B of the table together with those calculated from the equation $s = 2 \cdot 7 \cdot t^{0 \cdot 190}$. The original activity of the graphite was therefore in the main reproducible simply by heating and pumping off the gas.

III. The graphite, after a further 18 hours' vacuum-heating, was submitted (as cathode) to the electric discharge in hydrogen by connecting the platinum wires to the terminals of a powerful coil. The gas was rapidly taken up, some 3 to 4 c.c. disappearing in the course of 2 hours. The dead-space hydrogen was then pumped out in the cold (the absorbed gas showed no tendency to leave the graphite), and a third oxygen-sorption experiment was performed. The earlier results were again in agreement with the above form of equation, but the value of k required was about 12 times greater than previously. The deviations from the formula were small, even in the later stages, *in spite of the fact that the pressure had fallen almost to one-third of its initial value*. After the pressure had been again raised to near its original value, the deviations ultimately tended towards zero. The recorded sorption-values are given in Column C of Table I, together with the s-values calculated from the equation $s = 34 \cdot t^{0 \cdot 190}$.

The disappearance of the oxygen therefore showed all the characteristics of ordinary gas-sorption, its rate depending only to a relatively small extent on the pressure of the gas. Since the results of this experiment (in which the measuring system contained phosphorus pentoxide in close proximity to the graphite bulb) agree well with those of later ones (in which the measuring system contained no pentoxide), it follows that little water, if any, was disengaged during the reaction between the oxygen and the hydrogenated graphite. The highest sorption-value recorded represents about 4% of the hydrogen which had been driven into the graphite.

IV. Vacuum-heating for 72 hours now yielded some 200 c.mm. of permanent gas. Following this treatment the activity of the graphite towards oxygen was redetermined without further addition of hydrogen. The results, given in column D together with those calculated from the equation $s = 7 \cdot 8 \cdot t^{0 \cdot 190}$ indicate that, whilst the graphite was considerably more active than it had been originally, the greater part of its " induced " activity had been lost.

V. After a further protracted period of vacuum-heating the activity of the graphite towards carbon dioxide was tested both before and after the further addition of 2·3 c.c. (N.T.P.) of hydrogen under the influence of the discharge. The results of these experiments, which appear in columns E and F of the table, indicate that

the hydrogen, whilst perhaps exerting catalytic activity, had little influence on the amount of carbon dioxide ultimately taken up. Towards the end of the second experiment (hydrogen present in the

TABLE I.

Sorption values are expressed in cubic millimetres at N.T.P.

Time (mins.).	Oxygen. Hydrogen absent.				Oxygen. Hydrogen present.				Carbon dioxide. Hydrogen.		Oxygen. Hydrogen present.
	Initial.		Repeat.		Initial.		Repeat.		Absent.	Present.	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.			
	A.		B.		C.		D.		E.	F.	G.
1	1·9	2·9	2·7	2·7	34	34	4·9	7·8	1·9	4·5	—
2	3·6	3·3	3·5	3·1	39	39	6·9	8·9	2·0	5·4	—
3	3·6	3·6	—	—	42	42	—	—	2·0	5·7	34
4	—	—	3·7	3·5	45	44	—	—	2·4	6·2	—
5	4·3	4·0	—	—	47	46	8·9	10·6	—	6·2	39
6	—	—	—	—	48	48	—	—	—	—	41
8	—	—	—	—	51	51	—	—	—	6·2	—
10	—	—	4·2	4·1	53	53	12·1	12·1	2·8	6·4	45
13	—	—	—	—	55	55	—	—	—	—	—
15	—	—	4·2	4·4	57	57	12·8	13·0	—	—	48
20	6·0	5·1	4·4	4·7	61*	62*	14·0	13·8	3·9	—	52
30	—	—	—	—	64	66	15·0	14·9	—	—	56
40	6·4	5·8	5·2	5·3	67	69	15·7	15·7	5·7	—	59
50	—	—	—	—	69	72	—	—	—	—	61
60	—	—	—	—	—	—	17·1	17·0	—	—	63
70	6·7	6·6	—	—	73	77	—	—	—	—	65
80	—	—	5·7	6·1	—	—	17·9	17·9	6·7	—	69
100	7·3	7·0	—	—	77	81	—	—	6·8	6·4	72
150	7·5	7·5	—	—	85	89	20·1	20·5	—	—	79
200	7·9	7·9	6·2	7·1	91	93	—	—	—	—	83
240	—	—	—	—	95	96	—	—	—	—	88
290	8·5	8·5	—	—	99	100	—	—	—	—	—
320	—	—	—	—	101	102	—	—	—	—	—
1160	—	—	—	—	—	—	32·0	30·0	8·6	7·8	—
1350	—	—	—	—	127	133	—	—	—	—	—

* In these cases *et seq.*, the time ordinates should read as follows : 23, 33, 43, . . . 1353.

graphite), a bulb which formed part of the measuring system was cooled in liquid air; the carbon dioxide could thus be recovered quantitatively from the graphite without heating, and, further, no carbon monoxide (or any other permanent gas) had developed in the system from the reducing action of the atomic hydrogen.

VI. Following the removal of carbon dioxide in the cold, the activity of the graphite towards oxygen was again determined; the results are given in column G of the table and will be referred to later.

It will be noticed that the equations used to obtain the calculated sorption values for oxygen all involve a common power of t, viz., $t^{0·190}$. This fact (which implies a constancy of ratio between the different s-values for equal times) is most surprising, since a

growing mass of evidence obtained in these laboratories points to the conclusion that whilst equations of the type $s = k \cdot t^b$ are applicable in a large number of cases of sorption, the index b is highly susceptible to changes in the past history of the solid, and to the presence or otherwise of minute amounts of impurity. It is indeed difficult to escape the conclusion that the original activity of the graphite towards oxygen was due more or less directly to the hydrogen which it contained on manufacture.

The Variation of the " Induced " Activity with the Amount of Absorbed Hydrogen.

Experiments were next carried out to determine the quantitative relation between the amounts of hydrogen driven into the graphite and the consequent " induced " activities of the solid towards oxygen. In order to eliminate as a variant the pressure of the oxygen, the original calibrated deadspace was replaced by a graduated burette connected at its lower end by rubber tubing to a mercury reservoir. As the gas disappeared, its pressure was maintained by raising the level of the mercury in the burette, the McLeod gauge serving mainly as a null instrument.

Since the hydrogen, once driven into the graphite, could not again be removed, it was necessary to use a fresh specimen of the powder for each experiment. In spite of the exercise of scrupulous care to ensure uniform vacuum-heat treatment for the different specimens, and of their withdrawal from a common stock of the ground-up material which had been thoroughly mixed, they showed remarkable differences in their original behaviour towards oxygen. For this reason, it was necessary to determine with some care the original activity of each sample.

The cause of this variation of original activity could not be traced. Experiments on separate samples of graphite, wherein the only known variant was the duration of the vacuum-heating, seemed to indicate that prolonged treatment reduced the activity towards oxygen. The " normal " treatment of 72 hours led to sorption values about 10% lower than those obtained after only 24 hours' vacuum-heating. On two occasions where the preliminary experiments yielded abnormally high sorption values, a repetition of the vacuum-heating gave normal results.

Seven series of experiments were carried out, the same quantity of graphite being used in each case, and the amounts of added hydrogen varying from 531 to 5290 c.mm. The detailed results of one of these, given in Table II below, will serve to illustrate the agreement between the observed sorption-values and those calculated from the equation $s = k \cdot t^{0.190}$.

TABLE II.

Sorption values are expressed in cubic millimetres (N.T.P.).

Time (mins.).	Preliminary experiment. No added hydrogen.		Final experiment. 5290 c.mm. (N.T.P.) of hydrogen added.	
	s obs.	⁑ calc.	*s* obs.	⁑ calc.
1	0·9	1·2	47	50
2	1·2	1·3	57	57
3	1·4	1·4	62	62
4	1·6	1·5	65	65
5	1·7	1·6	68	68
7	1·8	1·7	73	73
10	2·0	1·8	78	78
15	2·1	1·9	85	84
20	2·2	2·0	88	89
30	2·3	2·2	98	96
40	2·3	2·3	103	102
50	2·4	2·4	105	106
70	2·5	2·6	114	113
100	2·6	2·8	122	121
150	2·8	3·0	131	131
200	3·0	3·1		

In the absence of equilibrium data (presumably unattainable), the factor k forms the best available basis for comparing the activities of the graphite in the different experiments. The *increase* in the value of k, following the absorption of a given quantity of hydrogen, affords similarly a measure of the " induced " activity. In Table III these increments ($k_2 - k_1$) are compared with the amounts of added hydrogen (v in c.mm. at N.T.P.), and it is seen that the ratio $(k_2 - k_1)/v$ is nearly constant. The " induced " activity of the graphite is thus directly proportional to the amount of hydrogen driven into the graphite.

TABLE III.

v.	k_1. Before addn.	k_2. After addn.	$(k_2-k_1)/v$.	*v.*	k_1. Before addn.	k_2. After addn.	$(k_2-k_1)/v$.
531	0·9	5·2	0·0080	3675	3·5	37·3	0·0090
1062	6·3	13·7	0·0070	5290	7·0	41·3	0·0065
1856	5·3	19·6	0·0077	5290	1·2	50·1	0·0092
2645	1·9	22·4	0·0077				

The low value for the ratio $(k_2 - k_1)/v$ yielded by the penultimate series is undoubtedly connected with a modification of the normal procedure on that occasion, the graphite being allowed to stand over-night with the bulk of the hydrogen absorbed in it, and a small residue being added the next day before the oxygen sorption experiment.* That the " induced " activity of the graphite does slowly

* The normal procedure was to carry out the hydrogen absorption continuously, and to test the activity of the graphite towards oxygen on the same day.

decay was proved by a special experiment designed to test the point. At high temperatures, the decay is probably more rapid. On the other hand, the rate of decay appears to depend considerably on other circumstances, as is exemplified by the results of expt. VI. Although the full period of the carbon dioxide experiment (ca. 24 hours) elapsed between the absorption of hydrogen and the activity test with oxygen, the results of the latter, compared with those of the previous oxygen experiment, represent an increase of activity which corresponds exactly to the quantity of hydrogen absorbed. The ratio $(k_2 - k_1)/v$ amounts in this case to 0·0091.

Experiments in which the amount of graphite taken varied from 0·34 to 13 g. led to the conclusion that, at any rate between these limits, the " induced " activities were independent of the amount of the solid, and dependent only on the quantity of added hydrogen. Nevertheless, there are several objections to the view that the part played by the carbon is simply to maintain the hydrogen in its reactive state, so that it can combine with oxygen on admission of the latter. These are :

(1) Little water, if any, is disengaged during the process of the sorption, while on the other hand there is definite evidence that, on heating the " activated " material after prolonged exposure to oxygen, considerably more gas is evolved than if the exposure to oxygen is omitted.

(2) The " original " activity displays characteristics identical with those of the " induced " activity.

(3) The " original " activity of the graphite is reproducible (almost quantitatively) simply by submitting it to vacuum-heating.

(4) A specimen of Acheson graphite which had been exposed to the air for some years showed much the same (average) " original " activity as one fresh from the makers.

A simple explanation of the effect of the hydrogen-bombardment arises from a consideration of the crystal structure of graphite as determined by the X-ray method. According, for example, to Bernal (Proc. Roy. Soc., 1924, A, 106, 749), the carbon atoms lie in planes of successive nets of hexagons in such a way that whilst in any one plane they are extremely densely packed, the distance between successive planes is relatively great. The high degree of mutual saturation of the atoms in any one plane (comparable with that in benzene) renders the field between adjacent planes extremely weak, and hence it is that graphite is a poor " sorbent " and a good lubricant. We shall suppose that, unlike ordinary molecular hydrogen, the ions H^+ and H_2^+, projected with great energy against

the solid particles, are capable of entering into combination with the carbon to form C_xH_y. The mutual saturation of the carbon-carbon bonds being thereby destroyed, the absorption of hydrogen should effect somewhat similar changes of properties to those which accompany the reduction of benzene to dihydrobenzene. Absorption of H_2^+ would lead, in fact, to the formation of linkings of the ethylenic type, and that of isolated H^+ ions—if it occurred—to a still higher degree of unsaturation. Thus regarded, the fact that exposure to oxygen does not lead immediately to the formation and elimination of water need occasion no surprise, since the oxygen atoms would tend to add themselves to pairs of unsaturated carbon atoms.* The slow decay of the "induced" activity may reasonably be attributed to the tendency of the unsaturated carbon atoms to form conjugate systems.

The work of Debye and Scherrer (*Physikal. Z.*, 1917, 18, 291) and of Asahara (*Japan J. Chem.*, 1922, 1, 35) has made it clear that amorphous carbon (so-called) is essentially an agglomerate of extremely minute crystals which are graphitic in structure. The hydrogen content is, however, much greater than in graphite, and, quite apart from the question of its porosity, the greater sorptive activity of this substance is fully to be expected. The fact that the activities of different charcoals increase with their hydrogen content has been established by H. H. Lowry (*J. Amer. Chem. Soc.*, 1924, 46, 824). If the above explanation is correct, it is clear that the activity produced by a given proportion of hydrogen will depend very largely on its manner of distribution; also that many substances other than hydrogen should be capable of influencing the activity. The remarkable differences in "original" activity of the specimens of graphite indeed suggest that the activation could be brought about by other and simpler means than bombardment with hydrogen ions.

The possible influence of the gases (other than hydrogen) remaining sorbed in the graphite after its 72 hours' vacuum-heating has not been considered. Supposing these to consist largely of oxygen, it might be thought that the function of the hydrogen ions was simply to cause the removal of this as water, and so to permit a further quantity of oxygen to be taken up by the graphite on its exposure to that gas. It is certain, however, that no water or other

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* The question of the location, with respect to the surface of the solid, of the sorbed molecules in cases where the sorption obeys the formula $s = k \cdot t^b$ will be discussed in a future paper, together with that of the probable significance of this equation. It may be remarked, however, that the equation appears characteristic of "sorption" processes involving definite chemical reactions (such as are here considered) and not of the condensation in capillary spaces of vapours approaching saturation.

volatile substance was given off during the hydrogen-bombardment, since, on stopping the discharge and pumping out the deadspace hydrogen, no detectable gas whatsoever developed in the system on standing over long periods. Any water formed must, in fact, have been bound to the carbon complex about as tightly as its elements are in the case, for example, of the sugars. In some way or other, therefore, the primary valencies of the carbon atoms must be called upon, and the organic analogy would suggest that the first explanation is correct. The relatively gross quantities of hydrogen absorbed by the graphite under the discharge also warrant the conclusion that the absorption is due to direct combination with the carbon atoms.

CLII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXV. Three Optically Active Alcohols containing a Phenyl Group and some Esters derived therefrom.*

By LESLIE FRANK HEWITT and JOSEPH KENYON.

OF the optically active secondary alcohols that have already been examined, seven only have contained an aromatic radical. In optical properties, these seven alcohols contrast in several respects with alcohols of purely aliphatic character, and it was considered advisable to extend their number. Three optically active alcohols have therefore been prepared each containing a phenyl group, namely, β-phenylethylethylcarbinol, β-phenylethyl-*n*-propylcarbinol, and phenyl-β-phenylethyl carbinol. One of the most pronounced differences between an optically active alcohol containing a phenyl group and the corresponding aliphatic alcohol containing the same number of carbon atoms is that the rotatory powers of the former class are much greater than those of the latter. It may be noted, however, that the farther the phenyl group is removed from the asymmetric carbon atom in the following series of compounds, the smaller becomes its enhancing effect on the rotatory power.

Molecular Rotatory Powers, $[M]_D^{20°}$.

*CH_3·CH(OH)·Ph	50·9°	*CH_3·CH(OH)·CH_2Ph	36·1°
†CH_3·CH(OH)·$C_6H_{13}(n)$	12·7	†CH_3·CH(OH)·CH_2·$C_6H_{13}(n)$	12·9
	38·2		23·2
*CH_3·CH(OH)·CH_2·CH_2Ph	21·3°		
†CH_3·CH(OH)·CH_2·CH_2·$C_6H_{13}(n)$	13·7		
	7·6		
*CH_3·CH_2·CH(OH)·Ph	35·2°		
‡CH_3·CH_2·CH(OH)·$C_6H_{13}(n)$	10·6		
	24·6		
CH_3·CH_2·CH(OH)·CH_2·CH_2Ph	31·0°		
‡CH_3·CH_2·CH(OH)·CH_2·CH_2·$C_6H_{13}(n)$	10·7		
	20·3		

* Data given in Part VI, J., 1914, **105**, 1123.　† In Part I, J., 1911, **99**, 49.
‡ In Part IV, J., 1913, **103**, 1933.

Two further interesting points of difference arise when comparisons are made of the optical rotatory dispersions of these two series of alcohols. In the first place, the values of the rotatory dispersion $\alpha_{4358}^{20°}/\alpha_{5461}^{20°}$ for the members of the aliphatic series of alcohols are almost constant, lying between the narrow limits 1·63 and 1·66, whilst the corresponding values for members of the aromatic series of alcohols vary between 1·53 and 1·83. Furthermore, whilst the rotatory dispersions of the former class of compounds are only slightly affected by changes of temperature, those of the latter are very susceptible to this influence.

These aromatic alcohols show complex rotatory dispersion, since their rotatory powers cannot be expressed by a Drude equation of one term.

The absorption spectra of many aromatic compounds have been investigated (Baly, J., 1908, **93**, 1902), and in almost every case the spectra are described as being of some complexity and as containing at least one band nearer to the visible portion of the spectrum than $\lambda = 2500$ Å.U. An absorption band in this position corresponds, in a substance of simple dispersion, to a dispersion ratio $\alpha_{4358}/\alpha_{5461}$ of at least 1·85.* In the following table are given the values of this dispersion ratio for a number of aromatic secondary alcohols, and it will be observed that these all lie below this value. This is particularly the case with the alcohol which contains two phenyl groups in the molecule.

* When $\lambda_0 = 0·25$, $\lambda_0^2 = 0·0625$ and $a_{4358}/a_{5461} = (0·5461^2 - 0·0625)/(0·4358^2 - 0·0625) = 1·85$. It should be pointed out, however, that this calculation involves the assumption that the band of greater wave-length than $\lambda = 2500$ is a rotatory absorption band and not one which controls only the refractive dispersion.

P P*

Dispersion ratios ($\alpha_{4358}/\alpha_{5461}$) *at* 20° *for the alcohols in the homogeneous state.*

Phenylmethylcarbinol	1·736	β-Phenylethylethylcarbinol ...	1·695
Phenylethylcarbinol	1·687	β-Phenylethyl-n-propylcarbinol	1·757
Benzylmethylcarbinol	1·833	Phenyl-β-phenylethylcarbinol	1·533
β-Phenylethylmethylcarbinol	1·670		

A number of esters of the three optically active alcohols have been prepared and, in addition, three from *d*-β-phenylethylmethylcarbinol for purposes of comparison. The values of the rotatory dispersion ratio $\alpha_{4358}/\alpha_{5461}$ of these esters lie between the limits 1·78 and 2·51, except in the case of β-phenylethylmethylcarbinyl acetate, which has the very low value of 0·2 at 20°.

EXPERIMENTAL.

β-*Phenylethylethylcarbinol* (α-*Phenyl-γ-pentanol*).—A mixture of propionic and β-phenylpropionic acids was slowly passed over thoria at 420° and after removal of unchanged acids the resulting mixture of ketones was fractionally distilled. The phenylpentanone (b. p. 140°/14 mm.) thus obtained was reduced with sodium in moist ethereal solution, when the corresponding carbinol was readily obtained in good yield.

dl-β-*Phenylethylethylcarbinyl hydrogen phthalate* was obtained by heating a mixture of the carbinol and phthalic anhydride in molecular proportions at 110° for 15 hours and purifying the product in the usual manner. It crystallised from acetic acid in white prisms, m. p. 74°. 0·3996 G. required for neutralisation 29·3 c. c. of 0·0436N-NaOH; calc., for $C_{19}H_{20}O_4$, 29·35 c.c.

d- and l-β-*Phenylethylethylcarbinyl Hydrogen Phthalates.*—The *strychnine* salt of the *dl*-hydrogen phthalic ester was systematically crystallised from methyl alcohol–acetone. After six crystallisations, the strychnine salt *l*-B, *d*-A was obtained in a condition of optical purity: m. p. 158°, $[\alpha]_{5461}$ − 38·7° ($c = 5\%$ in chloroform solution). The more soluble fractions of the strychnine salt gave on decomposition a partly active hydrogen phthalic ester as a pasty mass which had $[\alpha]_{5461}$ − 15° in ethyl-alcoholic solution. Careful fractional crystallisation of this product from benzene–light petroleum yielded as the more soluble component a hydrogen phthalic ester with $[\alpha]_{5461}$ − 35° in ethyl-alcoholic solution. Five crystallisations from acetone of the *cinchonidine* salt of this highly active ester yielded the optically pure salt *l*-B, *l*-A in small, ill-defined crystals, m. p. 154°, which show $[\alpha]_{5461}$ − 54·2° ($c = 5\%$ in ethyl-alcoholic solution).

The *d*- and *l*-hydrogen phthalic esters were recovered from their corresponding alkaloidal salts in the form of colourless, viscous

gums which could not be induced to crystallise even when inoculated with the *dl*-ester of m. p. 74°. They show $[\alpha]_{5461} \pm 42\cdot9°$ ($c = 5\%$ in ethyl-alcoholic solution).

d- and l-β-*Phenylethylethylcarbinols* were obtained by heating the hydrogen phthalic esters with caustic soda solution and passing a current of steam. They distil at 143°/19 mm. and melt at 38°, whereas the *dl*-alcohol is a liquid.

β-*Phenylethyl*-n-*propylcarbinol* (α-*Phenyl*-γ-*hexanol*).—A mixture of *n*-butyric and β-phenylpropionic acids was passed over thoria at 425°. The phenylhexanone (b. p. 150°/20 mm.) isolated from the reaction mixture was reduced with sodium and moist ether, when the corresponding carbinol was obtained in good yield.

dl-β-*Phenylethyl*-n-*propylcarbinyl hydrogen phthalate*, obtained as described above, crystallises readily from many organic solvents in triangular prisms, m. p. 108°. 0·6343 G. required 21·8 c.c. of $0\cdot0886N$-NaOH; calc. for $C_{20}H_{22}O_4$, 21·9 c.c.

d- and l-β-*Phenylethyl*-n-*propylcarbinyl Hydrogen Phthalates*.—Fractional crystallisation of the very soluble *brucine* salt of the *dl*-hydrogen phthalic ester ten times from acetone gave the pure *l*-B, *l*-A salt, m. p. 95°, which has $[\alpha]_{5893} - 2\cdot1°$ ($c = 5\%$ in ethyl-alcoholic solution). Decomposition of the more soluble fractions of the brucine salt gave a partly active dextrorotatory hydrogen phthalic ester which after crystallisation from acetic acid gave as the more soluble fraction an acid ester of high dextrorotation. The crystallisation five times from acetone of the *brucine* salt of this dextrorotatory acid ester yielded the optically pure *l*-B, *d*-A salt, m. p. 75°, which shows $[\alpha]_{5893} - 12\cdot5°$.* The *l*- and *d*-hydrogen phthalic esters obtained from the respective brucine salts melt at 75° and have $[\alpha]_{5893} \pm 25\cdot5°$.

d- and l-β-*Phenylethyl*-n-*propylcarbinols* are volatile in steam, distil at 146°/16 mm., and form stellate clusters of prismatic needles, m. p. 34°. When crystals of the *d*- and *l*-carbinols are mixed, a liquid results.

Phenyl-β-*phenylethylcarbinol* (αδ-*Diphenyl*-α-*propanol*) has been described by Perkin (J., 1890, 59, 1008) and by Harries and Hübner (*Annalen*, 1897, 296, 325). A method based on that of the latter workers has been employed; benzylideneacetophenone in ethyl-

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* The curious observation was made that the rotatory powers of the *l*-brucine salt of the *d*-acid ester were of a higher lævorotation than those of the *l*-brucine salt of the corresponding *l*-acid ester. The following determinations were made in alcoholic solution ($c = 5\%$):

Salt.		$[\alpha]_\lambda$ 5893°	5461°	4358°	a_{4358}/a_{5461}
l-B,	*l*-A	$-$ 2·1°	$-$ 3·6°	$-$20·6°	5·7
l-B,	*d*-A	$-$12·5	$-$15·1	$-$38·6	2·5

alcoholic solution was reduced with sodium amalgam, hydrochloric acid being run in continuously to maintain the alkalinity at a minimum. A poor yield, never exceeding 25%, was obtained together with considerable quantities of the corresponding pinacol.

The carbinol (b. p. 200°/20 mm.) was obtained as a pale yellow, viscous oil containing a coloured impurity which is not easily removed by distillation. As mentioned later, it has been obtained as a white solid by hydrolysis of its purified hydrogen phthalic ester.

dl-*Phenyl-β-phenylethylcarbinyl hydrogen phthalate* was obtained by the method outlined above, as a white solid which crystallises from acetic acid in small, rectangular prisms, m. p. 110°. 0·4417 G. required 13·8 c.c. of 0·0886N-NaOH; calc. for $C_{23}H_{20}O_4$, 13·85 c.c.

d- and l-*Phenyl-β-phenylethylcarbinyl Hydrogen Phthalates.*— Five crystallisations from acetone of the *brucine* salt of the *dl*-ester yielded the pure *l*-B, *l*-A salt in hard, rectangular prisms, m. p. 121°, which show $[\alpha]_{5893} - 8\cdot8°$ ($c = 5\%$ in ethyl-alcoholic solution). The hydrogen phthalic ester recovered from the more soluble fractions of the brucine salt was converted into the corresponding *strychnine* salt. Fractional crystallisation of this salt five times from methyl alcohol rendered it optically pure. It forms hard needles, m. p. 189°, which are too insoluble in cold solvents for determinations of rotatory power to be made. The *d*- and *l*-hydrogen phthalic esters were obtained as viscous gums ($[\alpha]_{5893} \pm 8\cdot9°$) which could not be induced to crystallise.

d- and l-*Phenyl-β-phenylethylcarbinols* are not volatile in steam. Each distils at 195°/15 mm. and sets to a white, crystalline mass, m. p. 54°. Equal weights of the two carbinols were melted together and allowed to cool; the resulting inactive carbinol melted at 45·5° to a colourless liquid.

Esters of the Optically Active Alcohols.—The esters of the alcohols with fatty acids were prepared as follows : the *formates*—by heating the alcohol with excess of formic acid for $\frac{1}{2}$ hour at 100° ; *acetates* and *propionates*—by heating the alcohol with a molecular quantity of acetic or propionic anhydride, respectively, at 100° for an hour.

The alcohols recovered from each ester by hydrolysis were of unchanged rotatory power in each case.

Determination of the Physical Constants.—The determinations of density, made in a pyknometer of about 1·5 c.c. capacity, are given in Table V. All determinations of rotatory power of substances in the homogeneous state were made with a polarimeter fitted with a direct-vision spectroscopic eyepiece, the optically active liquid being contained in a 50 mm. jacketed tube, around which mineral oil was circulated. The following light sources were used : sodium and lithium flames and an enclosed mercury arc.

The figures given in Tables I and IV are taken from smooth curves obtained from the experimental figures given in Tables V and VI. The photographic determinations of rotatory power were obtained by using an open iron arc. A neon lamp and an open copper arc were used, in addition to the above-mentioned light sources, for the measurement of refractive indices.

TABLE I.
Specific Rotatory Powers of the Alcohols in the Homogeneous State at Different Temperatures.

$[a]_\lambda.$

Temp.	$d_{4°}^{t°}.$	6708.	5893.	5780.	5461.	4358.
			d-β-Phenylethylethylcarbinol.			
20°	0·9687	—	+18·95°	—	+23·00°	+38·98°
140	0·8773	—	18·70	—	23·30	39·98
			l-β-Phenylethyl-n-propylcarbinol.			
20°	0·9565	− 9·66°	−12·54	−13·18°	−15·06	−26·46*
140	0·8590	9·90	12·57	13·39	15·37	27·48
			d-Phenyl-β-phenylethylcarbinol.			
20° †	1·0661	+12·20	+16·12	+16·66	+18·95	+29·05
140	0·9640	14·87	18·63	19·34	21·68	35·16

* The following rotatory powers were determined at 20° by the photographic method : $[a]_{4342}$ −27·1°, $[a]_{4132}$ −31·4°, $[a]_{3950}$ −35·6°, $[a]_{3800}$ −39·7°.

† Certain of the values at 20° are extrapolated owing to the high melting point (54°) of the carbinol.

TABLE II.
Specific Rotatory Powers in Various Solvents at Room Temperature.

Solvent.	Grams of solute in 100 c.c. of solution.	6708.	5893.	5780.	5461.	4358.
				$[a]_\lambda.$		
			d-β-Phenylethylethylcarbinol.			
Benzene	4·8	—	—	—	+29·7°	+51·1°
Ethyl alcohol ...	5·0	—	26·8°	—	31·8	55·4
Carbon disulphide	5·2	—	30·2	—	35·4	62·9
			d-β-Phenylethyl-n-propylcarbinol.			
Benzene	4·9	+12·2°	+14·9	+16·3°	+17·6	+31·6
Ethyl alcohol ...	5·1	—	17·3	18·8	20·7	37·4
Carbon disulphide	5·2	—	21·9	22·7	25·0	46·2
			l-Phenyl-β-phenylethylcarbinol.			
*cyclo*Hexane	5·0	−15·3	−20·2	−20·8	−23·1	−38·0
Ethyl alcohol ...	4·6	−12·3	−15·6	−16·2	−17·9	−28·6
Carbon disulphide	4·8	−19·7	−25·4	−26·5	−30·4	−49·1
			l-β-Phenylethyl-n-propylcarbinyl hydrogen phthalate.			
Ethyl alcohol ...	4·6	—	−25·5	—	−30·1	−57·1
Chloroform	4·8	—	−18·2	—	−21·6	−39·6
Carbon disulphide	4·6	—	−39·8	—	−48·0	−93·1
			l-Phenyl-β-phenylethylcarbinyl hydrogen phthalate.			
Ethyl alcohol ...	5·1	− 7·6	− 9·0	− 9·8	− 10·4	− 9·8
Methyl alcohol ...	4·8	− 9·9	−12·1	−13·1	− 13·8	− 17·7
Chloroform	4·3	−20·0	−25·7	−26·2	− 30·6	− 49·3
Carbon disulphide	4·0	−72·0	−92·5	−96·5	−112·3	−209·0

TABLE III.

Refractive Indices of l-β-Phenylethyl-n-propylcarbinol at 20°.

λ ...	6708	5896	5790	5782	5461	5218	5153	5106	4358
$n_\lambda^{20°}$	1·5041	1·5085	1·5093	1·5093	1·5118	1·5139	1·5147	1·5151	1·5258

TABLE IV.

$$[M]_\lambda.$$

Temp.	$d_{4°}^{t°}$.	6708.	5893.	5780.	5461.	4358.
	d-β-Phenylethylmethylcarbinyl formate, b. p. 120°/15 mm.					
20°	1·0083	−25·10°	−35·50°	−37·09°	−42·90°	−81·56°
140	0·9119	−27·06	−36·92	−38·23	−43·90	−82·95
	d-β-Phenylethylmethylcarbinyl acetate, b. p. 130°/15 mm.					
20	0·9854	+ 2·92	+ 3·12	+ 3·14	+ 3·30	+ 0·63
140	0·8860	0·96	0·00	− 0·04	− 0·22	− 3·96
	d-β-Phenylethylmethylcarbinyl propionate, b. p. 141°/16 mm.					
20	0·9790	− 3·21	− 5·97	− 6·22	− 8·08	−20·23
140	0·8792	− 3·48	− 6·03	− 6·34	− 9·03	−21·61
	d-β-Phenylethylethylcarbinyl formate,* b. p. 135°/15 mm.					
20	0·9980	−32·74	−43·98	−46·33	−52·59	−98·34
140	0·8980	−27·88	−38·40	−40·62	−48·02	−86·38
	d-β-Phenylethylethylcarbinyl acetate,† b. p. 147°/19 mm.					
20	0·9829	−28·31	−38·27	−40·19	−46·76	−87·38
140	0·8825	−23·77	−31·29	−33·43	−38·67	−70·37
	l-β-Phenylethylethylcarbinyl propionate, b. p. 150°/14 mm.					
20	0·9731	+33·84	+46·11	+47·83	+55·31	+101·64
140	0·8703	26·99	35·90	37·16	43·63	78·98
	l-β-Phenylethyl-n-propylcarbinyl formate,‡ b. p. 147°/18 mm.					
20	0·9872	+34·52	+45·87	+47·93	+55·64	+101·70
140	0·8959	29·20	38·69	41·07	46·02	84·25
	l-β-Phenylethyl-n-propylcarbinyl acetate, b. p. 154°/20 mm.					
20	0·9725	+26·91	+36·65	+38·15	+43·34	+79·60
140	0·8750	22·37	29·77	30·98	35·55	61·93
	d-β-Phenylethyl-n-propylcarbinyl propionate, b. p. 163°/18 mm.					
20	0·9629	−28·94	−38·66	−40·72	−46·80	−85·82
140	0·8688	−23·52	−31·26	−32·88	−37·34	−67·16
	d-Phenyl-β-phenylethylcarbinyl formate, b. p. 195°/15 mm.					
20	1·0790	+68·16	+92·16	+96·79	+110·76	+196·80
140	0·9741	59·35	81·55	84·10	94·32	166·25
	d-Phenyl-β-phenylethylcarbinyl acetate, b. p. 165°/2 mm.					
20	1·0670	+103·3	+139·1	+144·7	+166·8	+297·8
140	0·9672	103·8	141·5	146·6	167·4	302·1

Additional Photographic Determinations at 20°.

* $[M]_{4810}$ −100·8°; $[M]_{4145}$ −112·3°; $[M]_{4035}$ −123·9°; $[M]_{3915}$ −135·4°.
† $[M]_{4222}$ −89·9°; $[M]_{3950}$ −119·5°; $[M]_{3850}$ −128·1°.
‡ $[M]_{4210}$ +106·4°; $[M]_{4190}$ +114·9°; $[M]_{4057}$ +127·6°; $[M]_{3925}$ +140·4°.

TABLE V.

Densities of Alcohols and Esters.

d-β-Phenylethylethylcarbinol (in fused state).
$d_{4°}^{t°}$ 0·9485 at 46·3°; 0·9288 at 72·5°; 0·9074 at 100·5°; 0·8832 at 131·5°.

l-β-Phenylethyl-n-propylcarbinol (in fused state).
$d_{4°}^{t°}$ 0·9588 at 17°; 0·9281 at 56·5°; 0·8982 at 93·3°; 0·8678 at 129·3°.

d-Phenyl-β-phenylethylcarbinol (in fused state).
$d_{4°}^{t°}$ 1·0228 at 70°; 1·0068 at 88·5°; 1·0046 at 92·5°; 0·9856 at 115°.

d-β-Phenylethylmethylcarbinyl formate.
$d_{4°}^{t°}$ 1·0132 at 14·5°; 0·9849 at 49·5°; 0·9553 at 86°; 0·9330 at 114·5°.

d-β-Phenylethylmethylcarbinyl acetate.
$d_{4°}^{t°}$ 0·9874 at 17°; 0·9451 at 68·5°; 0·9249 at 91°; 0·9042 at 117·5°.

d-β-Phenylethylmethylcarbinyl propionate.
$d_{4°}^{t°}$ 0·9851 at 13°; 0·9348 at 72°; 0·9194 at 91°; 0·8970 at 117°.

d-β-Phenylethylethylcarbinyl propionate.
$d_{4°}^{t°}$ 0·9997 at 17·8°; 0·9681 at 55°; 0·9416 at 86°; 0·9088 at 126·5°.

d-β-Phenylethylethylcarbinyl acetate.
$d_{4°}^{t°}$ 0·9863 at 15·3°; 0·9614 at 46°; 0·9256 at 88°; 0·8988 at 117·3°.

l-β-Phenylethylethylcarbinyl propionate.
$d_{4°}^{t°}$ 0·9723 at 20·5°; 0·9450 at 52·3°; 0·9209 at 81°; 0·8851 at 123°.

l-β-Phenylethyl-n-propylcarbinyl formate.
$d_{4°}^{t°}$ 0·9872 at 20·5°; 0·9606 at 56·5°; 0·9368 at 84·5°; 0·9209 at 105·5°.

l-β-Phenylethyl-n-propylcarbinyl acetate.
$d_{4°}^{t°}$ 0·9803 at 10°; 0·9436 at 56·5°; 0·9179 at 87·5°; 0·8923 at 118·5°.

d-β-Phenylethyl-n-propylcarbinyl propionate.
$d_{4°}^{t°}$ 0·9674 at 14·5°; 0·9397 at 45°; 0·9143 at 79·5°; 0·8920 at 109·5°.

l-Phenyl-β-phenylethylcarbinyl formate.
$d_{4°}^{t°}$ 1·0821 at 16·4°; 1·0473 at 56·5°; 1·0226 at 85°; 1·0016 at 114·5°.

d-Phenyl-β-phenylethylcarbinyl acetate.
$d_{4°}^{t°}$ 1·0709 at 15°; 1·0472 at 43°; 1·0198 at 78·5°; 0·9918 at 110°.

TABLE VI.

Observed Rotatory Powers in the Homogeneous State of a 50 mm. Layer of the Liquid.

d-β-Phenylethylethylcarbinol (in fused state).

α_{5893} +9·14° at 52·5°; 9·10° at 65°; 9·02° at 72°; 9·01° at 92·5°; 9·00° at 106·5°; 8·72° at 120·5°.

α_{5461} +11·09° at 52·5°; 11·08° at 64·5°; 11·06° at 72°; 11·01° at 93°; 10·99° at 106°; 10·73° at 121·5°; 10·26° at 139°.

α_{4358} +18·84° at 52·5°; 18·77° at 66°; 18·76° at 72°; 18·74° at 92·5°; 18·70° at 106°; 18·26° at 121°.

l-β-Phenylethyl-n-propylcarbinol (in fused state).

α_{6708} −4·64° at 22°; 4·70° at 45°; 4·57° at 88°; 4·35° at 120°; 4·24° at 142°.

α_{5893} −6·35° at 22°; 6·60° at 45°; 6·27° at 88°; 5·75° at 120°; 5·50° at 142°.

α_{5780} −6·35° at 22°; 6·60° at 45°; 6·53° at 89°; 6·04° at 120°; 5·75° at 142°.

α_{5461} −7·25° at 22°; 7·47° at 45°; 7·40° at 89°; 7·04° at 120°; 6·53° at 141°.

α_{4358} −12·73° at 22°; 13·12° at 49°; 13·00° at 89°; 12·52° at 120°; 11·69° at 141°.

<div align="center">Table VI continued.</div>

<div align="center">d-Phenyl-β-phenylethylcarbinol (in fused state).</div>

α_{6708} +6·99° at 62°; 7·35° at 88·5°; 7·55° at 106·5°; 7·43° at 120°.
α_{5893} +9·17° at 62°; 9·57° at 89·5°; 9·52° at 106·5°; 9·34° at 120°.
α_{5780}*+9·20° at 40°; 9·83° at 95·5°; 9·88° at 106·5°; 9·08° at 120°.
α_{5461}*+10·12° at 20°; 11·15° at 60°; 11·11° at 99°; 11·07° at 106·5°; 10·82° at 120°.
α_{4358}*+15·47° at 20°; 16·99° at 60°; 17·56° at 97°; 17·44° at 106·5°; 17·25° at 120°.

<div align="center">d-β-Phenylethylmethylcarbinyl formate.</div>

α_{6708} −7·39° at 20°; 7·40° at 53°; 7·36° at 93°; 7·28° at 112°; 7·13° at 128°.
α_{5893} −10·05° at 20°; 10·13° at 54°; 10·01° at 93°; 9·87° at 114°; 9·68° at 127°.
α_{5780} −10·51° at 20°; 10·70° at 55°; 10·49° at 94°; 10·30° at 115°; 10·00° at 128°.
α_{5461} −12·16° at 20°; 12·35° at 54°; 12·12° at 95°; 11·77° at 116°; 11·48° at 128°.
α_{4358} −25·09° at 20°; 23·38° at 54·5°; 22·58° at 95°; 21·90° at 118°; 21·58° at 128°.

<div align="center">d-β-Phenylethylmethylcarbinyl acetate.</div>

α_{6708} +0·75° at 16°; 0·60° at 63°; 0·45° at 96°; 0·40° at 112°; 0·36° at 120°.
α_{5893} +0·83° at 16°; 0·50° at 63°; 0·28° at 96°; 0·20° at 112°; 0·15° at 120°.
α_{5180} +0·84° at 16°; 0·47° at 63°; 0·27° at 96°; 0·18° at 112°; 0·10° at 120°.
α_{5461} +0·87° at 16°; 0·46° at 63°; 0·25° at 91°; 0·12° at 112°; 0·06° at 120°.
α_{4358} +0·16° at 16°; −0·35° at 63°; −0·57° at 90°; −0·75° at 112°; −0·82° at 120°.

<div align="center">d-β-Phenylethylmethylcarbinyl propionate.</div>

α_{6708} −0·76° at 14°; 0·85° at 60°; 0·84° at 96°; 0·82° at 112°; 0·80° at 126°.
α_{5893} −1·38° at 14°; 1·40° at 60°; 1·44° at 96°; 1·37° at 112°; 1·32° at 126°.
α_{5780} −1·46° at 14°; 1·54° at 60°; 1·52° at 96°; 1·45° at 112°; 2·00° at 126°.
α_{4358} −4·76° at 14°; 4·98° at 60°; 5·00° at 96°; 4·90° at 112°; 4·78° at 126°.

<div align="center">d-β-Phenylethylethylcarbinyl formate.</div>

α_{6708} −8·51° at 20°; 8·00° at 45°; 7·67° at 71·5°; 7·06° at 100°; 6·68° at 123°.
α_{5893} −11·43° at 20°; 10·90° at 46°; 10·30° at 71·5°; 9·61° at 100°; 9·02° at 123°.
α_{5780} −12·04° at 20°; 11·40° at 44·5°; 11·00° at 73·5°; 10·34° at 100°; 10·18° at 123°.
α_{5461} −13·93° at 20°; 13·16° at 44°; 12·66° at 71°; 11·91° at 100°; 11·50° at 123°.
α_{4358} −25·56° at 20°; 24·33° at 44·5°; 23·24° at 71°; 21·40° at 100°; 20·80° at 123°.

<div align="center">d-β-Phenylethylethylcarbinyl acetate.</div>

α_{6708} −6·78° at 18·5°; 5·82° at 81°; 6·29° at 48°; 5·46° at 107°; 5·32° at 122°.
α_{5893} −9·19° at 18·5°; 8·54° at 48°; 7·80° at 81°; 7·42° at 107°; 7·08° at 122°.
α_{5780} −9·75° at 18·5°; 9·02° at 48°; 8·38° at 81°; 7·96° at 107°; 7·50° at 123°.
α_{5461} −11·20° at 18·5°; 10·59° at 48°; 9·84° at 81°; 9·12° at 107°; 8·64° at 125°.
α_{4358} −20·91° at 18·5°; 19·49° at 48°; 17·99° at 81°; 16·62° at 107°; 15·93° at 124°.

* These measurements were made with the supercooled liquid.

TABLE VI *continued*.

l-β-Phenylethylethylcarbinyl propionate.

a_{6708} $+7.48°$ at $20°$; $6.84°$ at $49°$; $6.03°$ at $95°$; $5.80°$ at $109°$; $5.59°$ at $125°$.
a_{5893} $+10.20°$ at $20°$; $9.28°$ at $49°$; $8.68°$ at $77°$; $8.16°$ at $96°$; $7.38°$ at $125°$.
a_{5780} $+10.58°$ at $20°$; $9.55°$ at $49°$; $8.50°$ at $88°$; $8.05°$ at $109°$; $7.67°$ at $125°$.
a_{5461} $+12.23°$ at $20°$; $11.05°$ at $49°$; $9.86°$ at $92°$; $9.40°$ at $109°$; $9.00°$ at $125°$.
a_{4358} $+22.47°$ at $20°$; $20.21°$ at $49°$; $18.06°$ at $92°$; $17.30°$ at $109°$; $16.34°$ at $125°$.

l-β-Phenylethyl-*n*-propylcarbinyl formate.

a_{6708} $+8.08°$ at $19°$; $7.82°$ at $37°$; $7.31°$ at $70°$; $6.80°$ at $109.5°$; $6.54°$ at $124°$.
a_{5893} $+10.96°$ at $19°$; $10.54°$ at $37°$; $9.79°$ at $70°$; $9.01°$ at $109.5°$; $8.70°$ at $124°$.
a_{5780} $+11.46°$ at $19°$; $10.29°$ at $70°$; $9.58°$ at $98°$; $9.51°$ at $109.5°$; $9.21°$ at $124°$.
a_{5461} $+13.22°$ at $19°$; $12.65°$ at $46°$; $12.06°$ at $70°$; $10.92°$ at $109.5°$; $10.42°$ at $124°$.
a_{4358} $+24.28°$ at $19°$; $23.06°$ at $43°$; $21.78°$ at $70°$; $19.77°$ at $109.5°$; $19.02°$ at $124°$.

l-β-Phenylethyl-*n*-propylcarbinyl acetate.

a_{6708} $+5.98°$ at $17°$; $5.38°$ at $66°$; $5.12°$ at $71°$; $4.80°$ at $108°$; $4.62°$ at $129°$.
a_{5893} $+8.15°$ at $17°$; $7.24°$ at $66°$; $6.94°$ at $71°$; $6.50°$ at $108°$; $6.11°$ at $129°$.
a_{5780} $+8.50°$ at $17°$; $7.61°$ at $66°$; $7.20°$ at $71°$; $6.76°$ at $108°$; $6.32°$ at $129°$.
a_{5461} $+9.65°$ at $17°$; $8.69°$ at $66°$; $8.53°$ at $71°$; $7.69°$ at $108°$; $7.30°$ at $129°$.
a_{4358} $+17.73°$ at $17°$; $15.68°$ at $66°$; $15.07°$ at $71°$; $14.03°$ at $108°$; $12.84°$ at $129°$.

d-β-Phenylethyl-*n*-propylcarbinyl propionate.

a_{6708} $-6.03°$ at $16.4°$; $5.23°$ at $64°$; $5.01°$ at $88°$; $4.69°$ at $112°$; $4.55°$ at $124°$.
a_{5893} $-8.07°$ at $16.4°$; $7.16°$ at $62°$; $6.61°$ at $88°$; $6.24°$ at $112°$; $6.01°$ at $124°$.
a_{5780} $-8.48°$ at $16.4°$; $7.59°$ at $61°$; $7.02°$ at $89°$; $6.54°$ at $112°$; $6.33°$ at $124°$.
a_{5461} $-9.76°$ at $16.4°$; $8.57°$ at $64°$; $8.08°$ at $89°$; $7.53°$ at $112°$; $7.34°$ at $126°$.
a_{4358} $-17.88°$ at $16.4°$; $15.95°$ at $62°$; $14.37°$ at $87°$; $13.60°$ at $112°$; $13.19°$ at $125°$.

l-Phenyl-β-phenylethylcarbinyl formate.

a_{6708} $-15.48°$ at $14°$; $14.43°$ at $60°$; $13.85°$ at $83°$; $13.16°$ at $105°$; $12.66°$ at $123°$.
a_{5893} $-20.92°$ at $14°$; $19.38°$ at $60°$; $18.62°$ at $83°$; $17.67°$ at $105°$; $16.86°$ at $123°$.
a_{5780} $-21.90°$ at $14°$; $20.40°$ at $60°$; $19.60°$ at $83°$; $18.52°$ at $105°$; $17.92°$ at $123°$.
a_{5461} $-25.10°$ at $14°$; $23.24°$ at $60°$; $22.24°$ at $83°$; $21.14°$ at $105°$; $20.05°$ at $123°$.
a_{4358} $-44.75°$ at $14°$; $40.75°$ at $60°$; $38.87°$ at $83°$; $36.88°$ at $105°$; $35.28°$ at $123°$.

d-Phenyl-β-phenylethylcarbinyl acetate.

a_{6708} $+21.72°$ at $13°$; $21.56°$ at $44°$; $21.12°$ at $80°$; $20.67°$ at $102°$; $20.22°$ at $126°$.
a_{5893} $+29.29°$ at $13°$; $28.95°$ at $43°$; $28.40°$ at $79°$; $27.96°$ at $102°$; $27.36°$ at $125°$.
a_{5780} $+30.51°$ at $13°$; $30.08°$ at $45°$; $29.47°$ at $79°$; $29.01°$ at $103°$; $28.36°$ at $126°$.
a_{5461} $+35.13°$ at $13°$; $34.67°$ at $45°$; $33.97°$ at $79°$; $33.37°$ at $104°$; $32.47°$ at $127°$.
a_{4358} $+62.73°$ at $13°$; $61.92°$ at $45°$; $60.81°$ at $79°$; $59.63°$ at $104°$; $58.29°$ at $127°$.

TABLE VII.

Refractive Indices of the Esters at 20° for Light of Various Frequencies.

λ.	β-Phenylethylmethylcarbinyl			β-Phenylethylethylcarbinyl		
	formate.	acetate.	propionate.	formate.	acetate.	propionate.
6708	1·4934	1·4968	1·4906	1·4298	1·4849	1·4809
6402	1·4946	—	1·4916	1·4944	1·4861	1·4821
6096	1·4965	—	1·4934	1·4962	1·4880	1·4838
5896	1·4978	1·5012	1·4947	1·4973	1·4890	1·4850
5882	1·4978	—	1·4947	1·4974	1·4890	1·4850
5790	1·4986	1·5021	1·4953	1·4979	1·4896	1·4856
5782	1·4986	1·5021	1·4954	1·4980	1·4896	1·4856
5700	1·4992	1·5026	1·4960	1·4985	1·4902	1·4861
5461	1·5011	1·5044	1·4978	1·5003	1·4920	1·4878
5218	1·5032	1·5068	1·4999	1·5024	1·4940	1·4898
5153	1·5040	1·5076	1·5006	1·5032	1·4947	1·4905
5106	1·5045	1·5081	1·5012	1·5037	1·4951	1·4909
4358	1·5153	1·5186	1·5113	1·5141	1·5051	1·5004
4046	1·5217	1·5253	1·5179	1·5204	—	1·5059

Refractive Indices of the Esters at 20°.

λ.	β-Phenylethyl-n-propyl-carbinyl			Phenyl-β-phenylethyl-carbinyl	
	formate.	acetate.	propionate.	formate.	acetate.
6708	1·4884	1·4824	1·4808	1·5526	1·5306
6402	1·4898	1·4832	1·4821	—	—
6096	1·4915	1·4849	1·4839	—	—
5896	1·4925	1·4863	1·4848	1·5584	1·5451
5882	1·4925	1·4863	1·4849	—	—
5790	1·4932	1·4870	1·4855	1·5590	1·5456
5782	1·4933	1·4870	1·4855	—	—
5700	1·4939	1·4877	1·4860	—	—
5461	1·4957	1·4894	1·4877	1·5624	1·5497
5218	1·4977	1·4915	1·4896	—	—
5153	1·4983	1·4921	1·4903	—	—
5108	1·4984	1·4926	1·4907	—	—
4358	1·5089	1·5019	1·5000	1·5818	1·5664
4046	1·5148	1·5079	—	1·5913	—

CLIII.—*The Thermal Decomposition of Ammonia upon Various Surfaces.*

By CYRIL NORMAN HINSHELWOOD and ROBERT EMMETT BURK.

FROM the examples of hydrogen iodide (Bodenstein, *Z. physikal. Chem.*, 1899, **29**, 295), ozone (Chapman and Jones, J., 1910, **97**, 2463), chlorine monoxide (Hinshelwood and Prichard, J., 1923, **123**, 2730), and nitrous oxide (Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, *A*, **106**, 284), it is extremely probable that the thermal decomposition of ammonia would be bimolecular if it took place homogeneously. The homogeneous change has not been actually observed. In the experiments of Bodenstein and Kranendieck ("Nernst-Festschr.," 1912, p. 99), made in a vessel of quartz glass at 780° and 880°, the reaction observed was entirely a wall reaction, whilst in those of Perman and Atkinson (*Proc. Roy. Soc.*, 1904, **74**, 110), made in vessels of porcelain at higher temperatures, the nature of the observed reaction is not clear.

Recent experiments have shown that although the homogeneous decomposition of nitrous oxide is bimolecular, the catalytic decomposition on the surface of platinum and gold is unimolecular (Hinshelwood and Prichard, this vol., p. 327; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211), being resolved into the stages $N_2O = N_2 + O$, $2O = O_2$. In a similar way, it might be expected that, although the reaction $NH_3 = N + H + H_2$ or $NH_3 = N + 3H$ could not take place homogeneously, catalytically active surfaces would render it possible by adsorbing the atoms of hydrogen and nitrogen until they evaporate as molecules with others of their kind. There is abundant evidence of the affinity of metal surfaces for atomic hydrogen and oxygen. Nitrogen may well be similar in this respect.

We have made a study of the thermal decomposition of ammonia with the objects of finding whether the homogeneous reaction can be observed, and of investigating the kinetics of the catalytic reaction of various surfaces. The reaction was studied under the following conditions :

(*a*) In a vessel of fused silica at higher temperatures than those employed by Bodenstein and Kranendieck, up to 1050°.

(*b*) On the surface of a heated platinum wire, between 933° and 1215°.

(*c*) On the surface of a heated tungsten wire, between 631° and 941°.

In all cases equilibrium corresponds to almost complete decomposition of the ammonia. The general results of the investigation were as follows.

(1) Up to the highest temperature reached, 1050°, in a silica vessel, no sign of the homogeneous reaction was observed.

(2) The observations made on the reaction at silica surfaces were in general agreement with those of Bodenstein and Kranendieck, but the investigation of certain discrepancies between the two sets of observations led to some interesting conclusions about the mode of adsorption of ammonia, namely, that it is probably adsorbed on silica by means of its hydrogen atoms, and that the adsorption is very sensitive to the exact spacing of the silica molecules.

(3) Tungsten is the most efficient catalyst; the reaction at its surface is almost of zero order with respect to ammonia, and uninfluenced by the products of reaction. This catalyst is extremely constant in activity.

(4) The reaction on surfaces of platinum and silica is of the first order with respect to ammonia, and strongly retarded by hydrogen. The retarding influence of the hydrogen obeys a different law in the two cases. On platinum we have approximately

$$- d[NH_3]/dt = k[NH_3]/[H_2],$$

while on silica

$$- d[NH_3]/dt = k[NH_3]\{1 - c[H_2]\}.$$

(5) The retarded reaction on platinum has a very much greater temperature coefficient than the very much more rapid and unretarded reaction on tungsten, indicating that the temperature coefficient of the former reaction is largely determined by the freeing of the surface from hydrogen as the temperature increases.

Thermal Decomposition of Ammonia in a Silica Vessel.

A complete solution of the problem must elucidate the following points :

(1) The order of the reaction with respect to ammonia.

(2) The law according to which the retarding action of the products of reaction is exerted.

(3) The influence of temperature on the reaction velocity. In the ammonia decomposition, this appears to be a very complex matter. These points may be taken in order.

The experimental method was simply to measure the increase in pressure attending decomposition. In the experiments of Bodenstein and Kranendieck, corrections had to be made for the diffusion of hydrogen through the walls of the bulb. This was found unnecessary with the bulbs used in our experiments, partly because the actual diffusion of hydrogen per unit time was less and partly because the experiments nearly all occupied much less time.

The ordinary method of determining the order of a reaction is to find the influence of initial concentration upon the time required for the reaction to proceed to a given fraction of the way to completion. But when a reaction is retarded by the products, the order may easily be shown to be reduced owing to their influence. This may be explained as follows. Suppose the rate of decomposition to be expressed by the equation $dx/dt = k[NH_3]^n . f[\text{products}]$. Now if the products are very strongly adsorbed, so that the surface is almost completely covered as soon as their pressure attains quite a small value, then it can easily be shown that the amount of free surface where the ammonia can react is inversely proportional to the pressure of the products. Thus $dx/dt = k[NH_3]^n/[\text{products}]$. Integration of this equation shows that the observed order of the reaction would now be not n, but $n - 1$. Therefore, before assuming that the observed order of the reaction is actually the order with respect to ammonia we must know something about the degree of adsorption of the products.

The observed order of the reaction, obtained from the effect of initial pressure upon the time of half change, is nearly equal to one. This is illustrated by the following figures obtained when the bulb was in a fairly constant condition.

	T (abs.).	Initial pressure (mm.).	Time of half change (secs.).	T (abs.).	Initial pressure (mm.).	Time of half change (secs.).
Bulb I.	1264°	330	50	1220°	117	196
	1267	137·5	44	1220	298	191
	1268	325	57	1220	120	184
	1268	53·5	43			

The experiments are recorded in the order in which they were made. The same fact is illustrated by reading off the initial rate of reaction.

		Initial pressure. p_0.	$\left(\dfrac{\Delta p}{\Delta t}\right)_0$	$\dfrac{1}{p_0}\left(\dfrac{\Delta p}{\Delta t}\right)_0 \times 10^5$.		Initial pressure. p_0.	$\left(\dfrac{\Delta p}{\Delta t}\right)_0$	$\dfrac{1}{p_0}\left(\dfrac{\Delta p}{\Delta t}\right)_0 \times 10^5$.
Bulb II.	(1)	296	0·30	101	(2)	104	0·088	85
T (abs.).	(3)	259	0·24	93	(5)	92	0·075	82
1313°	(6)	239	0·19	80	(7)	75	0·073	97
	(4)	209	0·18	86				

The numbers in brackets indicate the order in which the determinations were made. The comparative constancy of the figures in the last column makes it clear that under these conditions the reaction can be regarded as empirically of the first order.

Retarding Influence of the Products.—Bodenstein and Kranendieck found that the products of the reaction had a retarding influence.

Our experiments confirmed this even at 1300° Abs.   If the reaction products are strongly adsorbed from the very beginning of the reaction, then the observed order will be less than the true order with respect to ammonia.   But in the equation $dx/dt = k[NH_3]^n f[\text{products}]$ we cannot, from observation of the velocity of the reaction at different points on the reaction–time curve, determine $f[\text{products}]$ unless we first know n.   (Attempts to determine this function with any precision by determining the initial velocity of the reaction for a constant pressure of ammonia, and varying the pressure of nitrogen and hydrogen previously introduced, were frustrated by the variability of the bulb surface.)   There is thus a vicious circle which can only be broken by a method resembling successive approximation.   We assume first that the order of reaction determined empirically in the last section is the true order, namely, that n is 1.   From the experimental values of p and t throughout a given experiment, we obtain values of $\Delta p/\Delta t$ over small ranges and the corresponding mean values of the pressures of ammonia and the products of the reaction.   Then $1/p_{NH_3} \cdot \Delta p/\Delta t$ is the rate of reaction corrected for the changing concentration of ammonia, assuming that n is 1.   This is proportional to the surface left uncovered by the products of the reaction.   We now plot $1/p_{NH_3} \cdot \Delta p/\Delta t$ against the pressure of the products.   Figure 1 illustrates the type of result found, the diminution of surface being almost a linear function of the pressure of the products over a very considerable range, indeed until the surface is reduced almost to zero.   If $V = 1/p_{NH_3} \cdot \Delta p/\Delta t$, then it follows that over a large range $V = V_0(1 - c[\text{products}])$.   The following figures illustrate this : $p = $ average pressure of the products, $V_{\text{obs.}} = \dfrac{1}{p_{NH_3}} \cdot \dfrac{\Delta p}{\Delta t} \times 1000$, and $V_{\text{calc.}}$ is calculated from the formula $V_{\text{calc.}} = 1 \cdot 35(1 - 0 \cdot 0054p)$.

p	12	32	52	72	86	101	121	141
$V_{\text{obs.}}$	1·31	1·08	1·02	0·85	0·69	0·61	0·50	0·32
$V_{\text{calc.}}$	1·27	1·11	0·97	0·86	0·74	0·63	0·47	0·32

The quantity $(1 - cp)$ gives the fraction of the surface left free for a given pressure of the products.   The important observation was made that c was independent of the temperature.   Thus the following values were obtained :

T (abs.)	1267°	1267°	1268°	1220°	1196°	1163°	1064°
$c \times 10^5$	455	455	375	435	423	540	418

Thus, under the conditions of these experiments, the retarding action of the products is independent of the temperature over a range of 200 degrees.

By assuming that n is 1, we have thus arrived at the equation

$$dx/dt = k[NH_3](1 - c[\text{products}])$$

or

$$dx/dt = k(a - x)(1 - cx).$$

It now remains to be seen whether, taking this equation as a first approximation, the value of n inferred from the influence of pressure on the time of half change needs modification.

FIG. 1.

Increase in p (*proportional to concentration of* H_2).
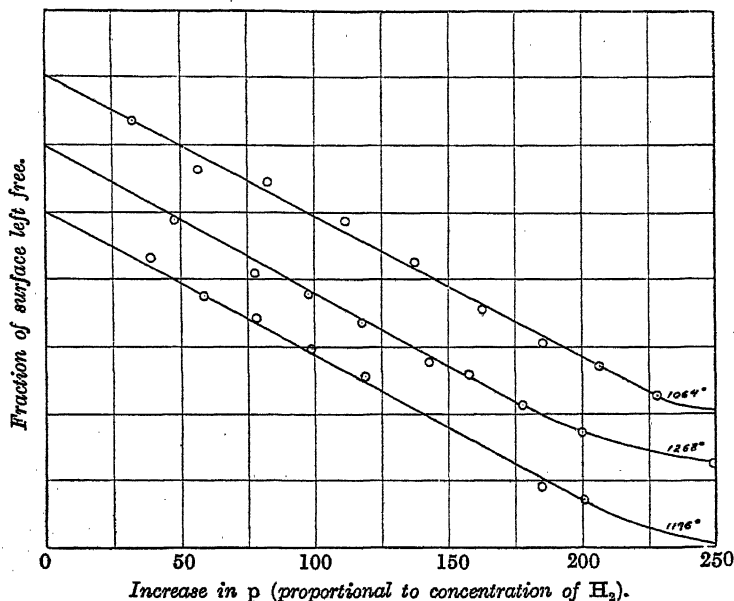
The divisions of the vertical scale are 0·2   *The three curves are each drawn from a different origin (taken as* 1·0 *in each case) to avoid superposition.*

The integrated form of the above equation is

$$t = \frac{1}{k(1 - ca)} \log \frac{(1 - cx)a}{(a - x)}$$

and if

$$t = \tau \text{ when } x = a/2$$

then

$$\tau = \frac{1}{k(1 - ca)} \log 2(1 - 1/2ac).$$

Putting $c = 0.004$, we have, for $a_1 = 200$ mm., $\tau_1 = 0.91/k$
and for $a_2 = 100$ mm., $\tau_2 = 0.82/k$.

Thus the half life according to this equation should not remain quite steady when the pressure is reduced from 200 mm. to 100 mm., but should decrease by 10%. This, however, would not have been

enough to vitiate the conclusion that n is 1. The first approxim-
ation may therefore stand as sufficiently correct.

The relation between the pressure of the products and the amount
of surface covered is not without interest. Up to 200 mm., which
is not very far removed from the saturation limit, the adsorption
isotherm of the reaction products is nearly linear, after which it
bends sharply round and tends slowly towards saturation. The
silica bulb used by Bodenstein and Kranendieck showed a quite
different adsorptive capacity, and one which varied greatly with
temperature, since they found the retarding action of the products

Fig. 2.
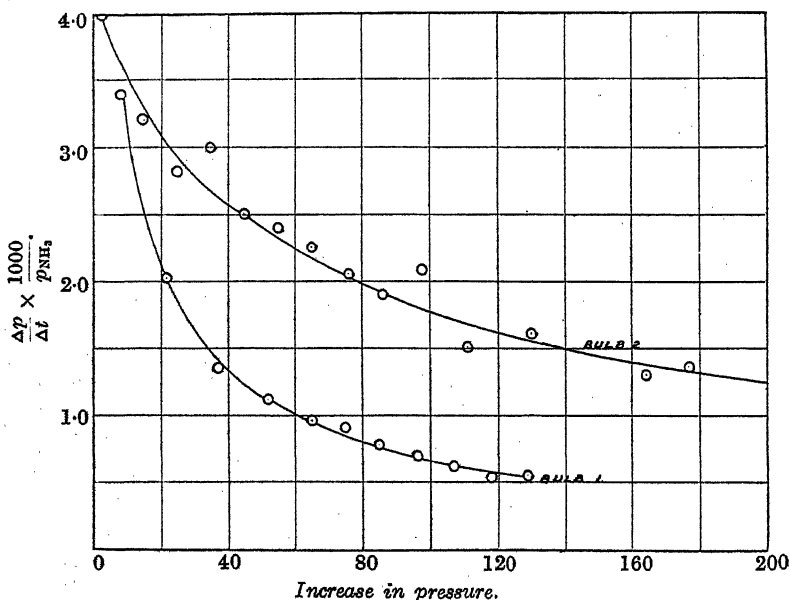
to be considerably greater at low temperatures than at high tem-
peratures, whilst in the present experiments, the retarding influence
is nearly independent of temperature.

At first, this difference in behaviour seemed rather surprising,
but prolonged observation of one bulb through the course of
seventy-five experiments, and the comparison of the two bulbs
showed how remarkably variable the adsorptive capacity of the
surface could be. Thus after bulb I had been used for about fifty
experiments, including all those so far quoted, the character of its
adsorption curve underwent a considerable change, assuming the
form shown in Fig. 2. During two or three experiments the curves
were of a transition type. This may have been associated with a

slow devitrification of the surface, but is probably due to a more subtle change in the configuration of the surface, since a completely new bulb also yielded adsorption curves of this form.

The great sensitiveness of the silica in regard to adsorptive capacity explains another striking difference between the present results and those of Bodenstein and Kranendieck. These observers state that while nitrogen and hydrogen together retard the reaction, nitrogen and hydrogen separately exert no retarding influence. This seems very remarkable and quite inexplicable, and repetition of the experiment failed to confirm the result. Hydrogen added to the bulb was found to have as strong a retarding action as the products of the reaction acting jointly. Thus the following are some typical results :

T (abs.).	Initial pressure of ammonia.	Initial pressure of hydrogen.	Initial pressure of products from a previous experiment.	Time of half change in seconds.
1196°	288	0	—	140
1194	302	200	—	515
1194	306	0	—	116
1195	222	200	—	304
1321	293	—	0	15
1323	290	—	0	13
1321	292	—	100	38
1321	298	—	200	31
1321	285	—	0	10
1226	278	0	—	90
1225	248	200	—	547
1226	280	0	—	61
1225	219	100	—	424
1225	201	200	—	844

The very marked retarding action of added hydrogen is sufficiently evident, and is clearly of the same order as that of the products of the reaction. The hydrogen was pure electrolytic hydrogen from a cylinder. The explanation of the discrepancy seems to be as follows. The mixture of nitrogen and hydrogen which Bodenstein and Kranendieck found to retard the reaction consisted of the reaction products left in from a previous experiment. These had been formed *in situ* on the surface, and under these conditions it would appear that the hydrogen remained adsorbed, whilst, when introduced from outside, it apparently did not readily attach itself to the surface. In view of the demonstrated sensitiveness of the silica surface, this seems quite possible, and indeed other examples of the phenomenon are known. Thus Freundlich (" Kapillarchemie," 2nd edition, p. 203) quotes some experiments of Zisch in which carbon monoxide actually produced by the decomposition of nickel carbonyl poisoned the surface of the nickel, whilst added carbon monoxide had no action. Fresh light came accidentally in

the course of the present series of experiments. Numerous fruitless efforts were made to obtain an exact relation between the amount of hydrogen added and the initial rate of reaction, but at this point the activity of the bulb, which had been fairly constant, began to vary too much to allow accurate results to be obtained. At last, the retarding effect of added hydrogen seemed to disappear altogether unless the added hydrogen was allowed to remain in the bulb for some time before the introduction of the ammonia. Bulb II showed the retarding effect of hydrogen as well as bulb I.

The Effect of Temperature.—Bodenstein and Kranendieck found the temperature coefficient of the reaction velocity to be very small, and to be different at different stages of the reaction. Thus between 780° and 880° the initial rate increased 1·3 times only. This ratio increased with the amount of decomposition products in the bulb, reaching a value of about 4·2.

With Bulb I the results found in the present investigation were in the sharpest contrast with this. The temperature coefficient was very high, and showed no systematic change over the course of the reaction. The following numbers illustrate the constancy :

| | | Time in seconds for the decomposition to reach | | | | | |
		10%.	20%.	30%.	40%.	50%.	60%.
1161° (Abs.)		73	184	310	543	746	1220
1064 „		280	630	1134	1773	2640	3660
	Ratio	3·9	3·4	3·7	3·3	3·6	3·0
1263 „		—	8	16	29	50	84
1219 „		—	40	90	180	312	484
	Ratio	—	5·0	5·6	6·1	6·2	6·8

Numerous other pairs of experiments showed sometimes a slight rise and sometimes a slight fall in the ratio.

This is in keeping with the experiments described above on the constancy of the adsorption of the products at various temperatures. Taking, therefore, the time of half change as the typical measure of the reaction rate, the following table shows the effect of the temperature on the reaction in bulb I. The usual straight line is obtained on plotting the logarithm of the time of half change against the reciprocal of the absolute temperature.

T (abs.)	1268°	1195°	1135°	1114°	1092°
Average τ in seconds ...	9	128	943	2430 .	7656

The rate of reaction increases nearly fifty times between 1100° and 1200° Abs.

There is no question of a homogeneous reaction surpervening, for in a second bulb at an equal temperature the reaction proceeded

at only a fraction of the rate observed in bulb I. Two examples will suffice.

	Bulb I (1268°).	Bulb II (1261°).
Time of half change (secs.)	9	790

The remarkable difference between the temperature influence in these experiments and in those of Bodenstein and Kranendieck led to the repetition of some of the experiments in this second bulb. The temperature coefficient was now only 2·6 for 100 degrees over the range 1250° to 1400° Abs., being thus double that observed by Bodenstein and Kranendieck (1·3), but in most striking contrast with that found for bulb I.

Initial Variations in the Activity of the Silica Surface.—In the first experiments made with bulb I its activity showed a marked and steady increase, and then remained constant for a long time. The initial increase could not have been due to progressive devitrification or other spontaneous change of the surface, since the bulb had been heated at 1318° for many hours before the first experiment, and then the whole series of eight determinations was carried out rapidly in quite a short time. Nor could the increase in activity have been due to reduction of the silica, since allowing the bulb to stand in contact with air did not remove the activity. It was concluded that the progressive increase must have been due to changes in the configuration of the surface caused by the actual process of decomposing ammonia.

Comparison with the Results of Bodenstein and Kranendieck and General Conclusions.—The main differences between the results of the two investigations are :

(1) Bodenstein and Kranendieck found that added hydrogen had no retarding influence, whereas it is now shown that it can have just as large a retarding influence as the products of the reaction formed *in situ*. This difference is attributed to the sensitiveness of the hydrogen adsorption to the exact configuration of the silica surface.

(2) Bodenstein and Kranendieck found the temperature coefficient to be very low, whereas we now find that it may have a very large value, but again is very sensitive to the exact nature of the surface.

(3) Bodenstein and Kranendieck found the retarding influence of the products to vary with temperature, whereas we have found that it can be constant over a range of 200 degrees. We find, however, that the shape of the adsorption isotherm of the products may undergo changes after prolonged use of the bulb.

These differences are not fundamental contradictions, and one of the principal points which emerges from the present investigation

is the extreme sensitiveness of the surface both with regard to activity in decomposing ammonia, and to the adsorptive capacity for the products of the reaction.   The adsorption equilibria must be extraordinarily delicately balanced in this case, and can be completely shifted by slight changes in the configuration of the surface.   A single example will show how this might be accounted for.   Suppose adsorbed ammonia molecules were held by two adjacent silica molecules.   At a higher temperature, the distance between adjacent silica molecules might have increased owing to changes in the exact configuration of the surface to such an extent that ammonia molecules could now be adsorbed only with great difficulty.   Thus the amount of ammonia in a position to react would have diminished and the naturally high temperature co-efficient of the rate of chemical change of the ammonia actually adsorbed would be reduced to an observed temperature coefficient with a quite low value.   Were, however, the silica molecules more closely packed to begin with, adsorption of the ammonia might occur just as readily at the higher temperature, and the normal "chemical" temperature coefficient would not be masked.   The remarkable fact that hydrogen formed in the reaction may remain adsorbed under conditions where hydrogen added to the bulb is not adsorbed seems to show that ammonia is adsorbed on silica by means of its hydrogen atoms.

Thermal Decomposition of Ammonia on a Heated Platinum Wire.

The apparatus used was identical with that used by Hinshelwood and Prichard for the catalytic decomposition of nitrous oxide. The temperatures were obtained from the resistance of the heated platinum wire, the temperature–resistance curve of a piece of the same wire being separately determined by comparison with a direct reading thermo-couple over the range of temperature used in the experiments.   The pyrometer itself was checked by taking the boiling point of zinc and the melting point of antimony.   Pure dry ammonia was used.   The high thermal conductivity of the hydrogen produced during the reaction renders it necessary to increase continuously the electrical energy supplied to the wire, in order to keep the temperature at its original value.   The energy supplied was controlled by a delicately adjustable rheostat so that the resistance of the wire remained constant throughout the experiment.

Kinetics of the Reaction.—Hydrogen has a marked retarding effect on the reaction, the rate being approximately inversely proportional to the amount of hydrogen present.   This is shown

by the following experiments carried out at 1138°, with 100 mm. initial pressure of ammonia in each case :

Pressure of hydrogen added (mm.)	50	75	100	150
Pressure (mm.) of NH₃ decomposed in 120 seconds	33	27	16	10

The reaction velocity seems to increase indefinitely as the pressure of hydrogen is reduced, as the following experiment shows :

Pressure of NH₃ 200 mm. $T = 1138°$.

Time (secs.)	10	60	120	240	360	720
Pressure (mm.) of NH₃ decomposed	28	56	72	89	100	120

The rapid falling-off in the rate of reaction as hydrogen is formed is evident. It is also clear that the actual rate of reaction during the first fraction of a second must be very great. These and the previous results justify one in assuming that approximately

$$- d[NH_3]/dt = k[NH_3]^n/[H_2] = k(a - x)^n/x.$$

This is quite different from the sort of retardation caused by hydrogen on a silica surface; where the rate of reaction is not inversely as the hydrogen pressure, but decreases linearly as the hydrogen pressure increases.

Nitrogen has practically no influence on the rate of reaction. Thus in one experiment at 1090°, 38% of the ammonia decomposed in 120 seconds in the absence of nitrogen and 40% in the presence of an equal volume of nitrogen.

The value of n in the velocity equation may be found as follows. If n is 1 in the above equation, it is easily shown that the time taken for a given fraction of ammonia to decompose is directly proportional to the initial pressure. This is approximately true. Thus we have at 1138° :

Initial pressure of ammonia (mm.).	Time required for decomposition of		
	40%.	50%.	60%.
100	90⎫	180⎫	330⎫
200	170⎭	360⎭	720⎭
Ratio	*1·9*	*2·0*	*2·2*

At a lower temperature the ratio of the times required for 20% decomposition was 1·83 for 100 mm. and 200 mm.

Influence of Temperature.—Experiments were made with ammonia at 100 mm. pressure. Each time an equal volume of hydrogen was added, since it is impossible to find the initial rate of reaction in the absence of hydrogen. The time taken for 20% of the ammonia to decompose is taken as a measure of the rate of reaction.

T (abs.)	1488°	1478°	1456°	1411°	1385°	1365°	1331°	1304°
Time in seconds (t)	18	44	55	110	306	1680	2040	7560

The best straight line drawn through the $(1/T)$, $(\log t)$ points gives a value for the heat of activation of approximately 140,000 calories.

It may be shown that where specific changes with temperature in the activity of the catalyst itself are not an important factor the apparent heat of activation in a retarded catalytic action of this type is approximately given by

Observed heat of activation = True heat of activation — heat of adsorption of reactants + heat of adsorption of retarding products.

The unusually high value found in this reaction must be attributed largely to the influence of the last term.

Thermal Decomposition of Ammonia on the Surface of Tungsten.

The reaction vessel used for these experiments consisted of a 32-volt Osram lamp, to which were sealed capillary tubes leading to the Gaede pump, to the ammonia supply, and to a mercury manometer, the volume of all connexions being negligible compared with that of the bulb. A battery of accumulators supplied the electrical energy. From the resistance of the wire while heated, its temperature was calculated using the data of Langmuir (*Physical Rev.*, 1916, 7, 159). The reaction bulb was kept in melting ice, the amount of decomposition being measured by the change in pressure measured at 0°.

The wire was remarkably constant in activity; decomposition of the ammonia took place at rather lower temperatures than on platinum or silica, and was uninfluenced by the presence of hydrogen. These points are shown in the following table :

Temperature 856° Time (secs.).	100 mm. NH_3. No H_2.	100 mm. NH_3. 100 mm. H_2.	100 mm. NH_3. No H_2.
		Mm. decomposed.	
100	13·5	14	13
200	23·5	24·5	23
300	33·5	34·5	33·5
400	42·5	.44	43
500	51	52·5	51·5
700	—	67	67
800	75	—	—
1000	87	—	—
1200	96	—	—
	100	—	—

The reaction is very nearly of zero order with respect to ammonia. The following table shows that when the absolute pressure of ammonia is increased fourfold, the absolute rate of reaction increases by about one-third only :

Temperature 856°. Time (secs.).	Millimetres decomposed. 200 mm. of NH₃.	50 mm. of NH₃.	Temperature 856°. Time (secs.).	Millimetres decomposed. 200 mm. of NH₃.	50 mm. of NH₃.
100	14	12	800	92	—
200	27	20	1000	112	—
300	38	28	1200	132	—
400	48·5	35	1400	149	—
500	59	—	1800	178	—
600	70	—	2000	187	—

The first experiment in the above table has two other points of interest. The progress of the reaction is much more nearly linear than monomolecular, for example, 70 mm. change in the first 600 seconds and 132 mm. in 1200 seconds. Moreover the portion of the curve representing the decomposition from 50% onwards coincides with the curve obtained with 100 mm. of ammonia. This is a satisfactory check on the adequacy of the method of temperature control, namely, working at constant resistance, since the electrical energy supplied in one case was nearly double that supplied in the other.

The effect of temperature was examined, and the results are summarised in the following table :

T (abs.).	Time (secs.) to reach 20% decomp. (t).	$\log_{10} t$.	$1/T \times 10^6$.
904°	14,300	4·155	1106
958	3,600	3·556	1044
1005	1,320	3·121	995
1068	425	2·628	936
1129	161	2·207	886

The curve obtained by plotting $\log t$ against $1/T$ is a very good straight line, the points lie on it closely enough to justify " point to point " calculation of the heat of activation from the formula

$$E = \frac{2\cdot303 \times 1\cdot98 \times \log_{10} t_1/t_2 \times T_1 T_2}{T_2 - T_1}.$$

Taking the values corresponding to 1129° as origin, the values of E calculated from the other four results are 37,900, 38,200, 38,800, 40,000. The average is 38,700 calories. This value is very much lower than that for platinum; this seems clearly to be connected with the absence of a retarding hydrogen film, the influence of which on the observed heat of activation was indicated in the last section.

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CLIV.—*The Labile Nature of the Halogen Atom in Organic Compounds. Part XI. The Halogenation of Ethyl Acetylsuccinate.*

By ALEXANDER KILLEN MACBETH and DAVID TRAILL.

IN previous papers it has been established that the halogen atom in the α-position in 1 : 3-ketonic esters is reduced by hydrazine, and the reaction has now been applied to the study of halogenated acetylsuccinic esters. Ruhemann and Hemmy (J., 1897, **71**, 330) found that the ethyl bromoacetylsuccinate they obtained by bromination of the parent ester in chloroform solution decomposed on distillation with the formation of ethyl bromide and ethyl ω-carboxy-α-methyltetronate. They therefore assigned the γ-bromo-structure to the ester, and this inference is supported by the present work, which shows that the bromo-ester similarly prepared liberates little nitrogen from hydrazine hydrate. Further, Wolff and Junker (*Annalen*, 1913, **399**, 309) have shown that when ethyl diacetyl-succinate is brominated in chloroform solution it also gives rise to the γ-bromo-derivative, for on heating the dibromo-ester ethyl bromide and bistetronic acid are obtained.

In the previous halogenations of 1 : 3-diketones substitution occurred between the two carbonyl groups, and the α-halogenation of acetylsuccinic ester was therefore to be expected. Direct γ-halogenation would necessitate a prior enolisation involving the methyl group, and such a change is improbable (Auwers and Auffenberg, *Ber.*, 1917, **50**, 929). It is now clear, however, that the formation of the γ-bromo-derivatives must be accounted for by the migration of the halogen atom from the α-position where it first enters : cases of such migration are well established in the acetoacetic esters (Hantzsch, *Ber.*, 1894, **27**, 356, 3169; Conrad, *Ber.*, 1896, **29**, 1042).

By chlorination with sulphuryl chloride the α-chloro-derivative of ethyl acetylsuccinate is obtained, for the product is reduced almost quantitatively by hydrazine hydrate with the liberation of nitrogen and the formation of ethyl 3-methyl-5-pyrazolone-4-acetate by the action of excess hydrazine on the reduction product.

Phenylhydrazine reacts with this chloro-ester in an interesting way. Schonbrodt (*Annalen*, 1889, **253**, 197) investigated the action of this reagent on chloro-, bromo-, and iodo-acetoacetic esters, and isolated a derivative which Buchka and Sprague (*Ber.*, 1889, **22**, 2548) proved to be 4-benzenehydrazo-1-phenyl-3-methyl-5-pyrazolone. The reaction with α-chloroacetylsuccinate, however, cannot follow a similar course, the necessary α-hydrogen atom being

lacking. The product contains no chlorine, and gives no characteristic ketonic reactions. One molecule each of phenylhydrazine and of the chloro-ester are involved in the reaction, which produces *ethyl β-carbethoxy-γ-benzeneazo-Δᵝ-pentenoate* (I) :

$$COMe \cdot CCl(CO_2Et) \cdot CH_2 \cdot CO_2Et \longrightarrow$$
$$CMe(:N \cdot NHPh) \cdot CCl(CO_2Et) \cdot CH_2 \cdot CO_2Et \longrightarrow$$
$$CMe(N:NPh):C(CO_2Et) \cdot CH_2 \cdot CO_2Et \quad (I.)$$
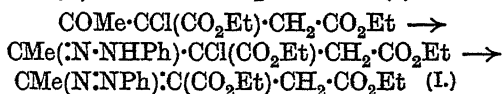
Support for this view is found in the formation of ethyl β-benzeneazocrotonate (II) from ethyl α-chloroacetoacetate and phenylhydrazine in ethereal solution (Bender, *Ber.*, 1887, **20**, 2747). On hydrolysis of the ester (I) an acid of the probable structure (III) is formed by loss of carbon dioxide.

$$\text{(II.)} \quad CMe(N:NPh):CH \cdot CO_2Et \qquad CMe(N:NPh):CH \cdot CH_2 \cdot CO_2H \quad \text{(III.)}$$
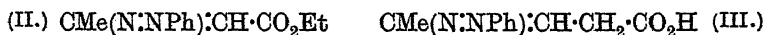
A good yield of the α-bromo-ester may be obtained if the bromination of ethyl acetylsuccinate is carried out in an aqueous solution of potassium hydroxide. Brominations previously carried out by introducing the halogen into an ester by means of a rapid current of air (Smith, *J. Amer. Chem. Soc.*, 1922, **44**, 216; Macbeth, J., 1923, **123**, 1122) gave in all cases the α-bromo-derivative. When acetylsuccinic ester is thus brominated, the product contains only some 26% of the α-bromo-ester. Migration of the halogen atom from the α- to the γ-position therefore occurs much more readily in this than in the case of the acetoacetic esters, the trace of hydrogen bromide present being sufficient to induce the change; and therefore it is not surprising that the γ-bromo-ester is formed during bromination in chloroform, where the hydrogen bromide formed is mostly retained.

The behaviour of ethyl chloro- and bromo-nitromalonates is of some interest in connexion with polarity and other views. These compounds do not possess the hydrogen atom necessary to give the *aci*-form of the salts, and the tendency to acquire such an atom must be regarded as a potential factor in the reactivities of the compounds. Ethyl bromonitromalonate is vigorously reduced by hydrazine hydrate, with the liberation of the theoretical volume of nitrogen and the elimination of the halogen atom (Hirst and Macbeth, J., 1922, **121**, 911). In contrast with this, the chloro-ester reacts without the evolution of any gas, giving the hydrazide of ethyl chloronitroacetate. Alcoholic ammonia reacts in a similar way, giving the corresponding ammonium salt.

In the first case, it is evident that the polarity effect manifests itself, the strongly positive bromine being removed; in the second case, where the halogen is not so positive, the tautomeric hydrogen is acquired by the elimination of a carbethoxy-group, the reaction

following a course somewhat similar to the removal of a carbethoxy-group from ethyl nitro*iso*succinate by alcoholic ammonia with the formation of the ammonium salt of ethyl *aci*-nitropropionate (Steinkopf and Supan, *Ber.*, 1910, **43**, 3245).

<div align="center">EXPERIMENTAL.</div>

Ethyl α-Chloroacetylsuccinate.—Ethyl acetylsuccinate, prepared by the addition of a slight excess of ethyl chloroacetate to dry ethyl sodioacetoacetate suspended in benzene, was obtained in good yield as an oil, b. p. 139°/12 mm.

Sulphuryl chloride (15 g.) was gradually added to 22 g. of the ester, hydrogen chloride and sulphur dioxide being briskly evolved, and the mixture was heated on a water-bath for $\frac{1}{2}$ hour. From the well-washed, dried (with sodium sulphate) ethereal solution of the product, *ethyl α-chloroacetylsuccinate* was obtained as a colourless oil, b. p. 140—142°/12 mm., n_D^{17} 1·4420 (Found : Cl, 13·7. $C_{10}H_{15}O_5Cl$ requires Cl, 13·8%).

Five c.c. of a solution (2·505 g. of the chloro-ester in 25 c.c. of alcohol), on treatment with hydrazine hydrate (50% solution), liberated 22·5 c.c. N_2 at 12·5°/754 mm., indicating the presence of 95·7% of the α-chloro-ester. The product of another experiment (5 g. of the chloro-ester in 10 c.c. of alcohol, and 50% hydrazine hydrate in slight excess) separated, on cooling, in small, glistening crystals which, twice crystallised from water, gave ethyl 3-methyl-5-pyrazolone-4-acetate in fine, silvery laminæ which appear as rectangular tables under the microscope, m. p. 166° (compare Curtius, *J. pr. Chem.*, 1894, **50**, 508).

Ethyl β-Carbethoxy-γ-benzeneazo-Δ^β-pentenoate (I).—Reaction between 10 g. of the chloro-ester, dissolved in alcohol (10 g.), and an excess of phenylhydrazine was started by warming. The solution gradually became deep orange-red, considerable heat being developed, and slowly solidified. The crystalline mass was washed with dilute spirit and recrystallised several times from 90% alcohol, the *pentenoate* separating in fine, lemon-yellow, rectangular needles, m. p. 188°. The compound is unchanged by treatment with an excess of phenylhydrazine in boiling alcohol (Found : C, 63·2; H, 6·4; N, 9·5. $C_{16}H_{20}O_4N_2$ requires C, 63·2; H, 6·6; N, 9·2%).

The ester (I) (3 g.) was boiled for 2 hours with 100 c.c. of 8% alcoholic potassium hydroxide, water added, and the alcohol removed under reduced pressure. The voluminous, orange-red precipitate obtained on acidifying the solution with hydrochloric acid was well washed with water, and, being difficult to purify by recrystallisation, was dissolved in alkali and reprecipitated by acid. The product dried in a desiccator to an orange-yellow solid,

m. p. 164—165° (decomp.), which was apparently the acid (III) (Found: C, 64·0; H, 5·3; N, 13·5. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9; N, 13·7%).

Ethyl α-Bromoacetylsuccinate.—To a cooled solution of 21·6 g. of ethyl acetylsuccinate in 100 c.c. of N-aqueous potassium hydroxide, a solution of 16 g. of bromine in 150 c.c. of methyl alcohol was added until the colour of the bromine was no longer discharged. The mixture was diluted with water, and the precipitated oil dissolved in ether. The ethereal solution was washed with very dilute sodium thiosulphate solution, dried with sodium sulphate, evaporated, and the residual oil distilled under diminished pressure; the main fraction, b. p. 144—146°/10 mm., $n_D^{17°}$ 1·4600, was ethyl α-bromoacetylsuccinate. Five c.c. of a solution (2·95 g. of the bromo-ester in 25 c.c. of alcohol), on treatment with hydrazine, liberated 19 c.c. N_2 at 13°/758 mm., corresponding with 81% of the α-bromo-ester.

The bromo-compound reacted with phenylhydrazine, but none of the product obtained in the case of the chloro-ester could be isolated. Heat was developed and the reaction mixture darkened to a deep orange-red; reduction seemed to occur, for nitrogen was evolved. On cooling, the mixture solidified to a crystalline mass of phenylhydrazine hydrobromide. In one experiment, a small quantity of the phenylhydrazone of ethyl acetylsuccinate, m. p. 85°, was isolated (Ruhemann, *loc. cit.*).

Ethyl γ-Bromoacetylsuccinate.—(a) Approximately the calculated quantity of bromine was vaporised and drawn with air through 15 g. of ethyl acetylsuccinate, cooled in ice. The bromo-ester obtained was washed repeatedly with dilute sodium thiosulphate solution and with water, dissolved in ether, dried with sodium sulphate, and the solvent removed. The residual oil (2·95 g.) was dissolved in 25 c.c. of alcohol; 5 c.c. of this solution liberated 6·3 c.c. N_2 at 21°/751 mm., which corresponds with an α-bromo-ester content of 25·9%. The ester decomposes on distillation.

(b) Bromine (8 mols.) reacted readily with ethyl acetylsuccinate in chloroform solution. The product was purified as described under (a), and the solvent was removed under diminished pressure. The residue oxidised hydrazine only to a slight extent, and so consisted mainly of the γ-bromo-ester.

Ethyl Chloronitromalonate.—Chlorine was passed into an aqueous solution of potassium *aci*nitromalonic ester (Wahl, *Compt. rend.*, 1901, **132**, 1052). The ethereal solution of the oil which separated was washed and treated as described above, *ethyl chloronitromalonate*, b. p. 127°/8 mm., being obtained on distillation (Found: Cl, 14·6. $C_7H_{10}O_6NCl$ requires Cl, 14·8%).

Hydrazide of Ethyl Chloronitroacetate.—When 50% hydrazine hydrate was added to an alcoholic solution of ethyl chloronitromalonate, scarcely any gas was evolved; but the mixture became warm, and soon filled with a mass of light yellow crystals. On recrystallisation from absolute alcohol, the hydrazide was obtained as a white solid, m. p. 120°. Under the microscope it appears as stellate masses of lath-like crystals (Found : N, 21·2 ; Cl, 17·9 ; N_2H_4, 16·15. $C_4H_{10}O_4N_3Cl$ requires N, 21·4 ; Cl, 17·9 ; N_2H_4, 16·0%).

Ammonio-derivative of Ethyl Chloronitroacetate.—When alcoholic ammonia was added to ethyl chloronitromalonate, the mixture became yellow, and soon changed to a crystalline mass. The product crystallised from 90% spirit in colourless needles, m. p. 115° (Found : N, 15·4 ; NH_3, 9·0 ; Cl, 19·3. $C_4H_9O_4N_2Cl$ requires N, 15·1 ; NH_3, 9·2 ; Cl, 19·3%).

Dilute sulphuric acid was added to an aqueous solution of the ammonio-derivative ; the resulting oil, isolated by means of ether, had b. p. 77—80°/8 mm. and n_D 1·4410. Ethyl chloronitromalonate has b. p. 77°/8 mm. and n_D 1·4412 (Macbeth and Traill, this vol., p. 895).

CLV.—*The Freezing Points of Hydrofluoric Acid.*

By JOHN DAVID CECIL ANTHONY and LAWSON JOHN HUDLESTON.

IN any case of equilibrium in solution, where the law of mass action is satisfied by the concentrations of the various ionic or molecular species, these concentrations must be proportional to the activities of the substances concerned or, better, equal to them, since the unit of activity for each substance may be arbitrarily defined. Hydrofluoric acid appears to offer such a case in solutions of exceptionally high concentration. Davies and Hudleston (J., 1924, **125**, 260) determined the composition of solutions of this acid by combining their measurements of the transference number with the conductivity data of Deussen (*Z. anorg. Chem.,* 1905, **44**, 312). Their results showed fairly good constancy for the expression $[HF_2']/[F'][HF]$ even up to twice (weight) normal solution, whilst the concentration of the undissociated hydrogen

fluoride was only about nine-tenths that stoicheiometrically present. Such a case offers an exceptionally favourable opportunity for comparison with the results of freezing-point determinations, from which the variation of activity of the hydrogen fluoride with changing concentration may be calculated directly, without recourse to any theory of dissociation.

In addition, it was desired to determine the activity of hydrogen fluoride in its aqueous solutions up to concentrations such that vapour pressure measurements are possible. The existing data of Paternò and Peratoner (*Atti R. Accad. Lincei*, 1890, **6**, 306, quoted from Abegg's "Handbuch") being rather scanty, the work described below was undertaken.

The method adopted was essentially similar to that of Adams (*J. Amer. Chem. Soc.*, 1915, **37**, 394). Two pure wax cylinders were almost filled with finely-crushed ice, water being added to one and solution to the other, the difference in temperature between them being measured by a thermo-element. Stirring was effected by means of inner wax cylinders with pierced bottoms, placed against the sides of the outer vessels and reaching from about 2 inches from the bottoms to within about the same distance of the tops of these. Closely fitting wax plungers, also pierced, could be moved up and down within the inner cylinders by means of heavily waxed copper rods. A disk of waxed lead foil above each plunger was free to slide up and down the central rod. This acted as a valve; on the down-stroke it readily lifted and allowed the solution to pass through the holes in the plunger, on the up-stroke it automatically closed these holes, so the liquid was continually drawn from the bottom and discharged again over the top. This stirring proved very efficient.

In the final form of the apparatus the outer wax cylinders were fitted with overlapping, water-tight wax lids, which carried vertical wax tubes for the plunger rod, the thermo-element, and for sampling. These lids were sealed into a metal case, a little larger than the wax cylinder, to make an air-jacket, and the whole was immersed, almost to the top of the tubes, in a bath kept at the temperature of the solution inside. The regulation of this, for the cylinder containing solution, was effected by means of a freezing mixture, water at room temperature being run in as required. The other cylinder required merely to be surrounded with crushed ice. With this arrangement, thermal equilibrium could be maintained for over an hour, but, just at the time this final form was evolved, the work had to be abandoned. The actual readings recorded were made with less efficient arrangements, only wax insulation being employed and the temperature of the outer bath being less

accurately regulated, and it is to this that the observed irregularities must be attributed. As there is no immediate prospect of repeating the work with the improved apparatus, and as it so happens that the curve is of such a form that the final results are not greatly vitiated, it seems worth while placing on record what has already been done.

The thermo-element, constructed similarly to that of Adams (*loc. cit.*), consisted of fifty copper-constantan junctions at each end, all being waxed. It was calibrated against a Beckmann thermometer in the same apparatus, the depressions being produced by potassium chloride. An ordinary cell potentiometer was adapted by using an auxiliary standard of about 0·05 volt (checked before and after each measurement) from a shunt in a high resistance circuit, and readings were made to 0·006° (0·003° for the very dilute solutions).

When equilibrium was established, a portion of the solution was withdrawn by means of a pure wax pipette and analysed by titration with sodium hydroxide, prepared by the method of Davies and Hudleston (*loc. cit.*) and standardised against benzoic acid.

The hydrofluoric acid for the dilute solutions was prepared as described by Davies and Hudleston (*loc. cit.*). The stronger solutions were prepared by treating potassium hydrogen fluoride with less than the theoretical amount of concentrated sulphuric acid in a platinum distilling flask. The side-tube of the flask was then sealed to a wax receiver, both being surrounded by ice-water, and the contents were distilled off from an oil-bath at 120°. The distillate contained more than 90% of hydrogen fluoride and was free from fluorosulphonic acid, since, after being diluted and boiled with bromine water, it gave no precipitate with barium chloride. Solutions were prepared from this by dilution, and the freezing points were consistent with those of solutions prepared by the other method.

The experimental results are recorded in Table I (where m is the molarity, mols. of hydrogen fluoride per thousand grams of water, and θ is the freezing point depression) and are shown graphically in the figures. Fig. 1 shows the whole range (with some of the data at low concentrations omitted for clarity), and in Fig. 1A the results in the more dilute solutions are shown on a larger scale. The general course of the curve is very nearly linear. This is of great assistance in tracing the best line through the somewhat discordant data; as a sinuous curve is highly improbable, the values at higher concentration check those at greater dilution. Thus the high points between M and $2M$-solutions cannot be reconciled with the remaining data without making the slope

first greater and then less, so their error is clearly indicated. The bend in the curve is sufficiently slight to be represented to a close approximation by a " smooth " curve composed of linear elements as drawn. This simplifies the calculation of activity changes, for if, for a given range of concentration, Δm, we have $\theta = Am + C$ (where A and C are constants), since $d \log_e a_2 = d\theta/\lambda m +$

FIG. 1A.   FIG. 1.
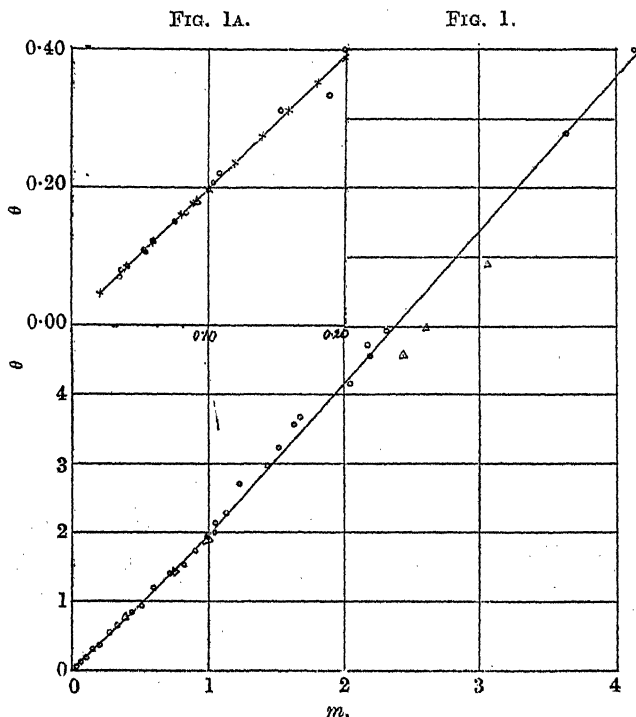
⊙ *Experimental.*   △ *Paternò and Peratoner.*   × *Theoretical.*

$0.00057\theta \cdot d\theta/m$ (Lewis and Randall, "Thermodynamics," 1923, p. 286), this becomes

$$d \log_e a_2 = A \cdot d \log_e m/\lambda + 0.00057\theta \cdot d\theta/m.$$

Changing to ordinary logarithms and noting that θ/m is sufficiently nearly 2 throughout, we get : $\Delta \log a_2 = A \cdot \Delta \log m/\lambda + 0.0005\Delta\theta$.

The data clearly cannot be extrapolated to zero on account of the dissociation of hydrofluoric acid, so it is necessary to define the activity arbitrarily for some one concentration. For reasons which will appear later, we have selected the value $a_2 = 0.0876$ when $m = 0.1$. Table II gives the result of the calculations for round molarities with the smoothed values of θ employed. It

might be emphasised that the activity coefficient, γ, given here is not the same as that usually employed for strong electrolytes, but is of the type used for non-electrolytes. Thus in dilute solution we should expect γm to be very nearly equal to the concentration of the undissociated hydrogen fluoride.

The values obtained by Paternò and Peratoner are also shown on the curves, marked as triangles. Their results agree closely with ours for dilute solutions, but are smaller than ours at the higher concentrations. These investigators used waxed glass vessels and, as we have found that wax very easily cracks at these temperatures, it is possible that contamination with silica occurred in their experiments, thus lowering the number of molecules actually present.

The order of accuracy is easily seen from the fact that the ratio of two activities is practically the ratio of the concentrations raised to the power A/λ, which varies from 1·023 to 1·196 in the curves as we have drawn them, from the lowest to the highest concentrations. With a total variation of only 7%, most of which is beyond question, there is little room for appreciable error and, except perhaps at the highest concentrations, a final accuracy of about 2% may be claimed. The activities may, however, have a considerable temperature coefficient for the stronger solutions, as the heat of solution of hydrogen fluoride in water is considerable. Thus they apply strictly only to the temperatures for which they were determined, the freezing points. In the analogous case of sulphuric acid, the change in activity on passing from the freezing point to 25° is negligible for solutions less than 0·1M and only 5% for M-solution (Lewis and Randall, *op. cit.*, p. 354), and this may be the order of magnitude in the present case.

Returning to the comparison with the concentration of the undissociated hydrogen fluoride determined by electrical measurements, we see, from the equation quoted above, that in dilute solution, if $a_2 = m$, $\theta = \lambda m$. Similarly, if a mixture of solutes be present to a total of n mols. per 1000 g. of water, and for each of them the activity is proportional to the molarity, then $\theta = \lambda n$.

On the assumptions previously used, we may calculate n for the case of hydrofluoric acid by solving (by successive approximation) the four equations (a) $[H^{\cdot}][F'] = K_1[HF]$, (b) $[HF_2'] = K_2[F'][HF]$, (c) $[H^{\cdot}] = [F'] + [HF_2']$, and (d) $m = [HF] + [F'] + 2[HF_2']$. No trustworthy data for K_1, and none at all for K_2, are known for 0°, but, as n is insensitive to their precise value, we have used the figures obtained by Davies and Hudleston at 25°, $K_1 = 7\cdot4 \times 10^{-4}$, $K_2 = 4\cdot7$, without fear of serious error. The values of λn resulting (shown as crosses on Fig. 1A) are entirely

compatible with the depressions determined experimentally for dilute solutions, definite divergence being hardly apparent before $m = 0.5$. This in particular supports the postulate that no appreciable quantity of double molecules exists. Moreover, this result, taken in conjunction with the conductivity and transference number data, considerably strengthens the general theory. Thus any attempt to explain the slowly diminishing molecular conductivity at solutions above $0.1M$ by the breakdown of the proportionality between active mass and concentration would almost certainly conflict with the results here given. According to the theory, the extra conductivity comes from the increasing quantity of complex ions, which do not affect the apparent molecular weight $(2HF = H^{\cdot} + HF_{2}')$, and $[F']$ does not increase with total concentration even as rapidly as it would do for a normal acid, and this is in accordance with the data.

The compositions of hydrofluoric acid solutions [calculated from equations (a)—(d)] at round molarities together with λn, the "theoretical" freezing-point depression, are given in Table III. It may be assumed with fair certainty that $a_{2} = [HF]$ in at least the dilute solutions and hence we have selected the value 0.0876 at $m = 0.1$. Below this, activities and activity coefficients are probably derived with more accuracy from these equations than by calculations from the freezing-point determinations.

Summary.

The freezing points of hydrofluoric acid have been determined for 0.025—$4M$-solutions, and the activities calculated. The postulate that hydrofluoric acid gives rise to complex ions, HF_{2}', in addition to simple ions has received confirmation, and the composition of the acid worked out on that assumption (together with that of the validity of the law of mass action applied to the concentrations) is supported. No appreciable amount of double molecules, $H_{2}F_{2}$, appears to exist.

TABLE I.

m	0·025	0·034	0·036	0·040	0·052	0·053	0·060	0·076
θ	0·056	0·069	0·078	0·085	0·108	0·107	0·123	0·150
m	0·082	0·100	0·104	0·109	0·154	0·190	0·201	0·259
θ	0·162	0·196	0·205	0·223	0·312	0·333	0·397	0·539
m	0·266	0·332	0·438	0·509	0·512	0·589	0·600	0·684
θ	0·494	0·642	0·840	0·948	0·954	1·104	1·182	1·320
m	0·694	0·719	0·758	0·812	0·819	0·849	0·865	0·901
θ	1·329	1·392	1·350	1·488	1·512	1·653	1·548	1·743
m	1·049	1·055	1·139	1·246	1·450	1·523	1·649	1·694
θ	1·986	2·117	2·250	2·697	2·958	3·219	3·567	3·648
m	2·056	2·187	2·203	2·331	3·649	4·140		
θ	4·131	4·692	4·553	4·895	7·783	8·990		

TABLE II.

m.	θ.	a_2.	$a_2/m=\gamma$.	m.	θ.	a_2.	$a_2/m=\gamma$.
0·10	0·196	[0·0876]	[0·876]	2·00	4·17	2·18	1·09
0·25	0·481	0·223	0·89	2·50	5·28	2·85	1·14
0·50	0·956	0·455	0·91	3·00	6·39	3·55	1·18
0·80	1·538	0·743	0·93	3·50	7·50	4·27	1·22
1·00	1·948	0·951	0·95	4·00	8·61	5·02	1·26
1·50	3·06	1·55	1·03				

TABLE III.

$m \times 10$.	[HF]$\times 10$.	[F']$\times 10^3$.	[HF$_2'$]$\times 10^3$.	[H·]$\times 10^3$.	[HF]/m.	θ.
0·2	0·161	3·3	0·3	3·6	0·805	0·043
0·4	0·339	4·7	0·7	5·4	0·848	0·083
0·6	0·518	5·6	1·4	7·0	0·862	0·122
0·8	0·698	6·2	2·0	8·2	0·872	0·160
1·0	0·876	6·8	2·8	9·6	0·876	0·199
2·5	2·222	9·0	9·4	18·4	0·889	0·482
5·0	4·467	10·3	21·6	31·9	0·893	0·949
8·0	7·15	11·0	37·0	48·0	0·894	1·507
10·0	8·94	11·3	47·4	58·7	0·894	1·880

The calculated activities at the higher concentrations may be expected to have a considerable temperature coefficient.

CLVI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part VI. Polyhydroxyflavylium Salts related to Chrysin, Apigenin, Lotoflavin, Luteolin, Galangin, Fisetin, and Morin.*

By DAVID DOIG PRATT and ROBERT ROBINSON.

IN Part IV (J. 1924, **125**, 200), we described methyl ethers of chrysinidin, apigeninidin and luteolinidin * and we now place on record a description of the corresponding phenols obtained on

* In September, 1924, I had the privilege of a discussion with Professor Willstätter in the course of which he explained that, for example, the name " morinidin " is to be preferred to " moridin," because it leaves open the possibility of denoting an anthocyanin, which may be found in nature and which gives morinidin on hydrolysis, by the name " morinin." For the sake of uniformity, we accept this suggestion, and replace the admittedly more euphonious names, apigenidin, luteolidin, and galangidin by the expressions which appear in the text. Professor Willstätter also informed us that he and his colleagues had synthesised galanginidin and morinidin chlorides which we had obtained at that time by a different method.—R.R.

demethylation of the salts in the usual manner. At the moment there is some dubiety in regard to the constitution of the pyrylium salts obtained by the condensation of benzoylacetaldehyde and its derivatives with phloroglucinol and this doubt affects the compound termed "*acacetidin chloride*" (Pratt, Robinson, and Williams, *loc. cit.*). The evidence at present available strongly suggests that this substance is 5 : 7-dihydroxy-4-anisylbenzopyrylium chloride and that it should therefore be named *epiacacetinidin chloride*. The compound described by Bülow and Sicherer (*Ber.*, 1901, **34**, 3896) as 5 : 7-dihydroxy-2-phenylbenzopyranol (1 : 4) hydrochloride and obtained by the condensation of phloroglucinol and benzoylacetaldehyde should be identical with chrysinidin chloride, but it is in fact quite different from this substance. The method which depends on the condensation of a derivative of salicylaldehyde with a substance containing the group –CO–CH$_2$– follows, however, an unambiguous course. Accordingly, we have adopted this process in order to obtain standard preparations of the flavylium salts of known constitution. 2-Hydroxy-4 : 6-dimethoxybenzaldehyde is condensed in presence of potassium hydroxide with acetophenone, 4-methoxyacetophenone, acetoveratrone, and 2 : 4-dimethoxyacetophenone to related chalkone derivatives, and these are all very readily converted by gently heating with mineral acids into pyrylium salts, from which chrysinidin (I), apigeninidin (II), lotoflavinidin (III), and luteolinidin (IV) chlorides are, respectively, obtained by demethylation with hydriodic acid followed by double decomposition of the iodides with silver chloride.
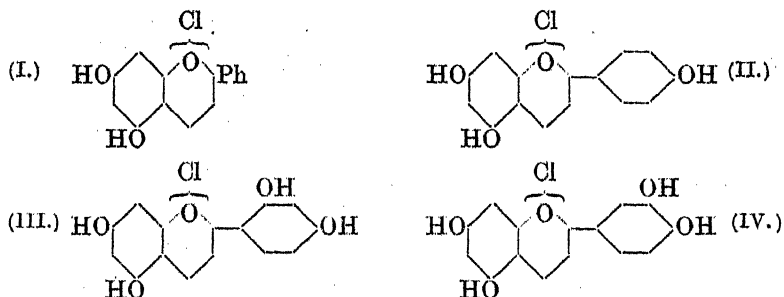
It is not necessary to adopt this indirect method in the case of ketones containing the group –CO–CH$_2$·OMe. Galanginidin chloride trimethyl ether (Part III, J., 1924, **125**, 195) and fisetinidin chloride trimethyl ether (Part V, this vol., p. 170) have already been described. Morinidin chloride pentamethyl ether is similarly obtained by condensation of 2-hydroxy-4 : 6-dimethoxybenzaldehyde with ω : 2 : 4-trimethoxyacetophenone by means of hydrogen

chloride in ethereal solution. By the usual methods we have now obtained galanginidin chloride (V), fisetinidin chloride (VI) and morinidin chloride (VII) (compare Willstätter and Schmidt, *Ber.*, 1924, **57**, 1945).
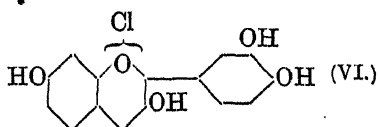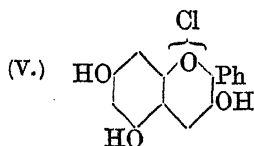
The colour reactions of these salts are of interest. Only (IV) and (VI) give the intense ferric chloride reaction characteristic of cyanidin, which confirms the theory that the necessary condition for a positive result in the test is the occurrence of hydroxyl groups in the ortho-position to one another. (I), (II), (III) and (IV) do not exhibit the property of pseudo-base formation, whereas (V), (VI) and (VII) are readily decolorised in dilute solution. This confirms our earlier statement of the effect of a hydroxy-group in position 3 on ease of pseudo-base formation (Part III, p. 748).

Fisetinidin (VI) closely resembles cyanidin in its behaviour with alkaline solutions and gives a pure blue coloration with aqueous sodium carbonate. On the other hand, luteolinidin (IV) gives a violet solution with sodium carbonate and this is changed to pure blue on the addition of sodium hydroxide. This behaviour throws some light on the constitution of certain anthocyanins. The researches of Willstätter and his co-workers have brought to light the existence of three types of diglucosides of cyanidin, represented by cyanin, mecocyanin and keracyanin.* With aqueous sodium carbonate, these yield blue, bluish-violet and reddish-violet solutions respectively, whilst, on the addition of sodium hydroxide, all give a blue solution. From our knowledge of the reactions of the less fully hydroxylated flavylium salts it is clear that in none of these substances can more than one hydroxyl group be combined with sugar residues and accordingly cyanin, mecocyanin and keracyanin must all contain a disaccharide unit.† The three anthocyanins mentioned give intense ferric chloride reactions and positions 3′ and 4′ therefore bear hydroxyl groups. This leaves the different colour reactions of cyanin, mecocyanin and keracyanin to be explained by the attachment of the carbohydrate to one of the positions 3, 5, and 7 in the cyanidin molecule and to a different

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* Keracyanin is a rhamno-glucoside, but the nature of the sugars does not appear to affect the colour reactions in alkalis.

† This is probably true of the majority of the anthocyanins which are diglucosides and is confirmed by the identity of the reactions of mecocyanin and chrysanthemin, the monoglucoside obtained by partial hydrolysis.

position in each of the three cases. Now the effect of combining a phenolic hydroxyl with a residue of a disaccharide is doubtless greatly to reduce its auxochromic power and since cyanin so closely approaches cyanidin in its reactions it is evident that one of the hydroxyls at 3, 5, and 7 is of relatively small importance from the colour-producing point of view. The other two positions cannot be blocked without affecting the tinctorial power.

Fisetinidin and luteolinidin represent cyanidin with one hydroxyl group removed. The reactions of the former substance are scarcely distinguishable from those of cyanidin and this suggests that the unimportant hydroxyl is the one situated at position 5 and that cyanin chloride has the constitution (VIII). This is confirmed by

(VII.) $(C_{12}H_{21}O_{10})O$ (VIII.)
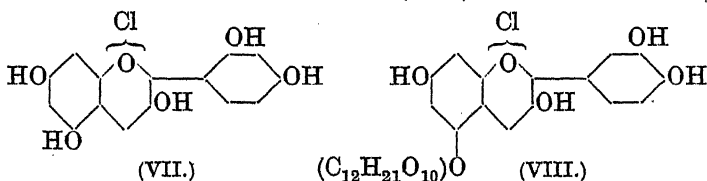
the fact that luteolinidin shows the behaviour with alkalis characteristic of keracyanin and mecocyanin. The soundness of this argument depends on the correctness of the deduction that mecocyanin and keracyanin have free hydroxyl groups in different positions. If the reddish-violet and bluish-violet reactions described as characteristic of solutions of keracyanin and mecocyanin, respectively, in aqueous sodium carbonate represent an unimportant difference, then in each case the sugar residue may be attached to oxygen in position 3 or in position 7 (but not in position 5, 3', or 4'). The expression (VIII) would then be a probable formula for cyanin chloride, but the possibility would remain open that the carbohydrate might be attached to oxygen in position 7 (but not in position 3, 3', or 4'). In order to gain further information on this subject the preparation of a flavylium salt with free hydroxyls in positions 3, 5, 3', and 4' is being attempted, but the problem proves to be a difficult one.

Morinidin chloride exhibits two noteworthy peculiarities. It cannot be recovered by acidification of its decolorised solutions and the pseudo-base evidently undergoes some further transformation. On reduction by warming with zinc dust in dilute hydrochloric acid solution, it yields a colourless solution which exhibits only a slight tendency to become coloured in contact with air. Ether extracts from this solution a colourless substance which dissolves in dilute aqueous sodium hydroxide to a most intense and beautiful blue solution which becomes brownish-green and then yellowish-brown on heating. Cyanomaclurin, $C_{15}H_{12}O_6$, isolated

by Perkin and Cope (J., 1895, **67**, 937) from Jak-wood (from *Artocarpus integrifolia* Linn.) dissolves in aqueous sodium hydroxide to a colourless solution which becomes deep indigo, then green and brownish-yellow on heating. It is much more than a mere coincidence that A. G. Perkin (J., 1905, **87**, 715) assigned to cyanomaclurin a constitution which is that of a dihydromorinidin and we believe that the substance obtained by reduction of morinidin chloride is probably identical with an early transformation product of cyanomaclurin under the influence of alkali. It differs from the latter in giving at once the deep blue coloration with sodium hydroxide. By moderating the conditions of reduction we hope to achieve a synthesis of cyanomaclurin. Finally, it should be mentioned that 5 : 7 : 3′ : 4′-tetramethoxyflavylium bromide is not identical with the substance of the same composition obtained from catechin tetramethyl ether by Drumm (*Proc. Roy. Irish Acad.*, 1923, **36**, 41). A direct comparison showed that the catechin derivative is related to a much weaker base than is the tetramethyl-luteolinidin salt and there is no resemblance whatever between the two substances. We are indebted to Dr. Drumm for a specimen which has enabled us to make this comparison.

EXPERIMENTAL.

Chrysinidin Chloride (I).—The direct condensation previously employed for the preparation of dimethylchrysinidin salts (Part IV, J., 1924, **125**, 201) gives unsatisfactory yields, and it is preferable to isolate a chalkone derivative in the first place. Potassium hydroxide (8 g.) dissolved in water (12 c.c.) was added to a solution of 2-hydroxy-4 : 6-dimethoxybenzaldehyde * (6 g.) and acetophenone (4 g.) in methyl alcohol (25 c.c.), and the mixture maintained for 12 hours at 60°. The cooled, diluted, red liquid was acidified with acetic acid, and the precipitated viscous mass washed with water and stirred with a little ether. The bright yellow solid was collected, washed with ether, and dried (5 g.). *Phenyl 2-hydroxy-4 : 6-dimethoxystyryl ketone* crystallises from alcohol in pale yellow, rectangular plates, m. p. 136°. The substance is coloured deep red in contact with concentrated hydrochloric acid but, on heating, a clear orange solution is obtained from which dimethyl-

* The technique which we employ in applying the Gattermann synthesis of hydroxyaldehydes is described in Part III (*loc. cit.*, p. 195). The quantities are the following : Phloroglucinol dimethyl ether (17 g.); ether (150 c.c.); potassium cyanide (17 g.), the last decomposed by means of a mixture of concentrated sulphuric acid (17 c.c.) and water (17 c.c.). The washed product was hydrolysed at 80° for 15 minutes. Yield of crystallised material, 15 g. Or anhydrous phloroglucinol (21 g.), ether (300 c.c.), and potassium cyanide (23 g.) were employed and 20 g. of 2 : 4 : 6-trihydroxybenzaldehyde obtained.

chrysinidin chloride separates in orange-red needles. The corresponding *iodide* crystallises from an aqueous solution in red, microscopic needles. The dry chloride (2 g.) together with phenol (8 g.) was added to hydriodic acid (50 c.c.; d 1·7), and the mixture boiled in a neutral atmosphere for 20 minutes. The cooled liquid after addition of water and ether deposited chrysinidin iodide in bright red needles (1·8 g.), and after isolation the substance was converted, by means of silver chloride in dilute hydrochloric acid solution, into chloride, which crystallised from hot dilute hydrochloric acid in orange-yellow needles (Found : in material dried in a vacuum over sulphuric acid, C, 58·1; H, 5·0. $C_{15}H_{11}O_3Cl,2H_2O$ requires C, 58·1; H, 4·8%). This salt darkens at 130°, but does not melt at 300°. It is readily soluble in the simple alcohols to a red solution and in acetone to an orange-yellow solution. The yellow solution in concentrated sulphuric acid exhibits a weak green fluorescence. The colour base obtained by the action of sodium acetate on the salt is red and dissolves in aqueous sodium carbonate to a red solution the colour of which is neither intense nor persistent on dilution. The chloride dissolves moderately readily in warm water to a red solution which contains colour-base and becomes orange on the addition of a trace of hydrochloric acid. The *perchlorate* crystallises from acetic acid in long, orange-yellow needles which darken at 178° and melt at 185° (decomp.).

Apigeninidin Chloride (II).—5 : 7 : 4'-Trimethoxyflavylium chloride (3·4 g.) (Part IV, *loc. cit.*, p. 205) and phenol (10 g.) were added to hydriodic acid (80 c.c.; d 1·7) and the mixture boiled during 25 minutes in a neutral atmosphere. On cooling, the demethylated iodide separated to some extent in slender needles, but a further quantity crystallised on the addition of ether (3 vols.) to the liquid. The salt was isolated (2·2 g.) and converted to chloride by means of silver chloride in dilute aqueous hydrochloric acid solution. The orange, microscopic crystals were obtained by recrystallisation from alcohol in short, red needles which darkened at 180° but did not melt at 300° (Found : in material dried in a vacuum over sulphuric acid, C, 54·9; H, 4·8. $C_{15}H_{11}O_4Cl,2H_2O$ requires C, 55·1; H, 4·6%). A film of this salt deposited on glass has a fine green lustre. The orange-red solution in alcohol exhibits a weak green fluorescence on great dilution, whilst the fluorescence of the yellow solution in sulphuric acid is bright. The chloride is moderately readily soluble in water to a red solution containing colour-base, but is sparingly soluble in dilute hydrochloric acid and invariably crystallises from hot solutions in slender needles. The colour-base obtained by the action of sodium acetate has a port wine red colour and the salt or this base dissolves in aqueous sodium

carbonate or ammonia to a rich damson solution. In presence of sodium hydroxide, the ring is easily broken and on acidification of the orange-red solution with acetic acid a chalkone is precipitated. Mineral acids readily reconvert the latter into the pyrylium salt. The *perchlorate* crystallises from acetic acid in small, orange-yellow, rectangular prisms which darken at 190°, soften at 220°, and decompose at 222°.

5 : 7 : 2′ : 4′-*Tetramethoxyflavylium Ferrichloride.*—A mixture of 2-hydroxy-4 : 6-dimethoxybenzaldehyde (4·5 g.), 2 : 4-dimethoxy-acetophenone (4·5 g.), methyl alcohol (30 c.c.), potassium hydroxide (8 g.), and water (10 c.c.) was maintained at 60° for 8 hours. After dilution the chalkone was precipitated with acetic acid; the oil, washed with water, solidified in contact with methyl alcohol. The substance (3·5 g. when dry) crystallised from methyl alcohol in pale yellow, rectangular prisms, m. p. 154°.

2 : 4-*Dimethoxyphenyl* 2-*hydroxy*-4 : 6-*dimethoxystyryl ketone* is sparingly soluble in alcohol or ether, forms a red potassium salt, and on boiling with concentrated hydrochloric acid, best in presence of a little acetic acid, is rapidly and quantitatively converted into 5 : 7 : 2′ : 4′-*tetramethoxyflavylium chloride*, which is sparingly soluble in moderately concentrated hydrochloric acid and crystallises in red needles which decompose at 134°. The *ferrichloride* is sparingly soluble in hot acetic acid and crystallises in slender, red needles which decompose at 180° (Found : C, 43·6; H, 3·8. $C_{19}H_{19}O_5Cl_4Fe$ requires C, 43·5; H, 3·6%). The yellow solution in sulphuric acid exhibits green fluorescence and this is also characteristic of the orange-pink *iso*amyl-alcoholic extract of an acid aqueous solution. The solutions are decolorised by sodium carbonate or sodium acetate.

Lotoflavinidin Chloride (III).—A mixture of hydriodic acid (50 c.c.; d 1·7), phenol (5 g.), and 5 : 7 : 2′ : 4′-tetramethoxyflavylium chloride (2 g.) was boiled for 30 minutes in an atmosphere of carbon dioxide. The red needles which separated on cooling, together with a quantity obtained by addition of water and ether to the mother-liquor, were isolated (1·6 g.). The chloride was prepared in the usual manner, but in alcoholic solution, and separated on cooling in orange-yellow needles which darkened at 190° but did not melt at 300° (Found : in material dried in a vacuum over sulphuric acid, C, 52·8; H, 4·4. $C_{15}H_{11}O_5Cl,2H_2O$ requires C, 52·6; H, 4·4%). The yellow solutions in the simple alcohols and in sulphuric acid exhibit green fluorescence. The salt is sparingly soluble in cold dilute hydrochloric acid, but in the hot solvent yields an orange solution. The colour-base is deep red and the alkaline solution is reddish-violet. Except for the loss of blue tinge, little change occurs on heating with sodium hydroxide

because the sodium salt of the related unsaturated ketone appears to be deeply coloured. The reactions of lotoflavinidin are intermediate between those of apigeninidin and luteolinidin, but more nearly resemble those of the former.

Luteolinidin Chloride (IV).—5 : 7 : 3′ : 4′-Tetramethoxyflavylium chloride (Part IV, p. 206) (1 g.) was demethylated in the usual manner and, after the addition of much ether, luteolinidin iodide (0·6 g.) separated from the hydriodic acid solution in red needles. Conversion into the chloride was carried out in alcoholic solution containing a little hydrogen chloride by warming with silver chloride for 10 minutes. The salt separated from the hot solution in reddish-brown clusters of prisms and it was observed that the crystallisation was retarded by the presence of water (Found : in material dried in a vacuum over sulphuric acid, C, 52·8; H, 4·7; Cl, 10·1. $C_{15}H_{11}O_5Cl,2H_2O$ requires C, 52·6; H, 4·4; Cl, 10·4%). The salt darkens at 200°, but does not melt at 300°. The alcoholic solutions are red with a violet tinge and devoid of fluorescence; in sulphuric acid the yellow solution exhibits a faint green fluorescence. Luteolinidin chloride is more readily soluble in water and dilute hydrochloric acid than is lotoflavinidin chloride; the aqueous solutions are coloured magenta, bluish-violet, and pure blue by sodium acetate, sodium carbonate, and sodium hydroxide, respectively. The intense reaction with ferric chloride is violet-blue in alcoholic solution and reddish-violet in aqueous solution.

Galanginidin Chloride (V).—A mixture of 3 : 5 : 7-trimethoxyflavylium chloride (Part III, p. 195) (1 g.), phenol (2 g.), and hydriodic acid (25 c.c.; *d* 1·7) was boiled for 15 minutes in a neutral atmosphere. Difficulty was experienced in isolating the iodide and on one occasion ether was added and after some days crystals were observed and the process of separation was then assisted by the addition of light petroleum. Golden-brown platelets (0·4 g.) were collected (Found : in air-dried material, C, 32·1; H, 3·1. $C_{15}H_{11}O_4I,HI,3H_2O$ requires C, 32·0; H, 3·0%). This compound, apparently a di-iodide, has m. p. 145°. In other cases, the hydriodic acid mixture was diluted with water and ether, and the iodide (0·4 g.) obtained as a red powder. The related *chloride*, obtained in the usual manner, crystallised from dilute hydrochloric acid in red needles which darken at 160°, but do not melt at 300° (Found : in material dried in a vacuum over sulphuric acid, C, 55·0; H, 4·8. $C_{15}H_{11}O_4Cl,2H_2O$ requires C, 55·1; H, 4·6%). Willstätter and Schmidt (*loc. cit.*) have described a dihydrate of this salt, but this lost $1H_2O$ in a desiccator. Perhaps the exposure was longer or the vacuum higher. The colour of the solutions of the salt and its reactions agree with those described by Willstätter and Schmidt,

except that we find that the addition of sodium carbonate to the solid salt gives a port wine-coloured solution. The colour is transient, and not very persistent on dilution. The yellow solution in sulphuric acid exhibits green fluorescence.

Fisetinidin Chloride (VI).—7-Hydroxy-3 : 3′ : 4′-trimethoxyflavylium chloride (3·6 g.) (Part V, this vol., p. 170) was demethylated by a boiling mixture of phenol (8 g.) and hydriodic acid (90 c.c.; d 1·7) in 30 minutes. The iodide crystallised on cooling and a further quantity was precipitated by the addition of ether (2 vols.). The isolated product (2·2 g.) was dissolved in alcohol (40 c.c.) containing a trace of hydrogen chloride and treated at 60° for 10 minutes with an excess of precipitated silver chloride. · Hydrochloric acid (25 c.c. of 7%) was added to the filtered solution, and the alcohol slowly removed by evaporation in a vacuum at the temperature of the room. Fisetinidin chloride crystallised in short, glistening, reddish-brown, prismatic needles with a violet sheen, and the process was repeated (Found : in material dried in a vacuum over sulphuric acid, C, 57·3 ; H, 3·9. $C_{15}H_{11}O_5Cl,0·5H_2O$ requires C, 57·1 ; H, 3·8%). On heating, the salt gradually darkens but does not melt. In colour reactions, it closely resembles cyanidin, although the red solution in alcohol is perhaps a little more scarlet-red. The ease of formation of pseudo-base, the ferric chloride reaction, and the behaviour with sodium carbonate are identical with the corresponding properties of cyanidin chloride. Fisetinidin chloride reduces Fehling's solution in the cold and gives a bluish-violet precipitate on the addition of lead acetate to an alcoholic solution. The points of contrast with cyanidin are the following : (1) Fisetinidin chloride does not melt if immersed in a bath at 220°. (2) Solutions of the violet colour-base have a redder tinge than those of cyanidin colour-base. (3) The blue coloration given with ferric chloride in alcoholic solution fades more rapidly in the case of fisetinidin. (4) The yellow-orange solution of fisetinidin salts in sulphuric acid exhibits an apple-green fluorescence which becomes dark green on standing. The orange-red solutions of cyanidin salts in sulphuric acid exhibit at first no fluorescence and a weak green fluorescence on standing. (5) The blue alkaline solutions are more unstable in the case of fisetinidin than in the case of cyanidin.

3 : 5 : 7 : 2′ : 4′-*Pentamethoxyflavylium Salts*.—Hydrogen chloride was passed through a solution of ω : 2 : 4-trimethoxyacetophenone *

· * This substance was obtained in improved yield in the following manner. Aqueous sodium hydroxide (40 c.c. of 20%) was added in one portion to a mixture of ω-methoxyresacetophenone (15 g.) and methyl sulphate (40 c.c.), which was then agitated but not cooled. Subsequently a further quantity

(2·5 g.) and 2-hydroxy-4 : 6-dimethoxybenzaldehyde (2·2 g.) in pure ether (30 c.c.) for 1·5 hours. Crystallisation from the crimson solution was induced by scratching, but only a small amount separated and the whole product was therefore diluted with water, the ether evaporated, and the mixture boiled and filtered. Clusters of red needles (1·2 g.) separated; a *ferrichloride* (0·5 g.) was obtained from the mother-liquor. The *chloride*, decomposing at 155°, crystallises readily from hot dilute hydrochloric acid in slender needles exhibiting a green reflex, but appearing red by transmitted light. The salt can be quantitatively recovered by addition of acid to decolorised solutions containing the pseudo-base. The *ferrichloride* crystallises from acetic acid in bright red needles which decompose at 194° (Found : C, 43·1 ; H, 4·0. $C_{20}H_{21}O_6Cl_4Fe$ requires C, 43·3 ; H, 3·8%). This derivative is readily soluble in the simple alcohols and also in chloroform to red solutions.

Morinidin Chloride (VII).—3 : 5 : 7 : 2' : 4'-Pentamethoxyflavylium chloride (1·7 g.) was mixed with phenol (5 g.), added to hydriodic acid (40 c.c.; d 1·7), and the whole boiled for 20 minutes in a neutral atmosphere. Water and much light petroleum were added and the precipitated black powder (probably a periodide) was collected (1 g.). Conversion into chloride was accomplished by means of silver chloride and a little silver in 10% hydrochloric acid, and the solution was boiled for only 5 minutes and then filtered. Longer treatment is disadvantageous. The chloride separated in a flocculent mass of slender needles which darkened at 100° and did not melt at 300° (Found : in material dried in a vacuum over sulphuric acid, C, 50·0 ; H, 4·4. $C_{15}H_{11}O_6Cl,2H_2O$ requires C, 50·3 ; H, 4·2%). Willstätter and Schmidt (*loc. cit.*) observed the formation of this hydrate, but again they noticed loss of $1H_2O$ in a desiccator. The description of morinidin given by these authors is, however, applicable to the salt we have prepared, especially in regard to the comparisons instituted with pelargonidin and cyanidin chlorides. The solubility of the salt is also in agreement with the description of Willstätter and Schmidt. The yellow solution of morinidin chloride in sulphuric acid exhibits only a weak green fluorescence. We have noticed that the blue alkaline solutions of many anthocyanidins are dichroic, and even if blue in thin layers or when dilute the colour is bluish-violet to reddish-violet to red in thicker layers or in greater concentrations. This dichroism is especially characteristic of alkaline solutions of morin-

of aqueous sodium hydroxide (50 c.c. of 20%) was introduced in about 3 portions. The oil solidified on cooling and was collected (13 g.); it crystallised from methyl alcohol in long, silky needles, m. p. 61° (compare Slater and Stephen, J., 1920, 117, 313).

idin. The interesting behaviour of morinidin on reduction is mentioned in the introduction.

One of us (D. D. P.) desires to thank the Carnegie Trust for a Fellowship which has enabled him to take part in this investigation.

THE UNIVERSITY, MANCHESTER.   [*Received, March 6th, 1925.*]

CLVII.—*The Action of Hydrogen Chloride on* cyclo-*Hexylideneazine and on* cyclo*Pentylideneazine.*

By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT.

A SHORT time since (J., 1924, **125**, 1503), we showed that *cyclo*-hexylideneazine (I) is converted into octahydrocarbazole (II) when its solution in tetrahydronaphthalene is treated with hydrogen chloride at 180°.

$$\text{(I.)} \longrightarrow \text{(II.)} + NH_3$$
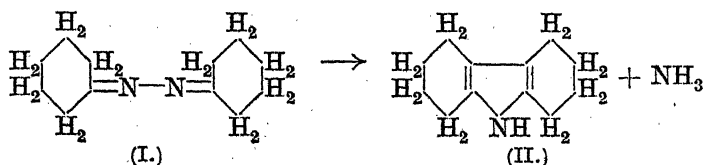
We have now investigated the action of hydrogen chloride under the same conditions on *cyclo*hexylidene*cyclo*pentylideneazine (III) and on *cyclo*pentylideneazine (IV), but in neither case has a pyrrole derivative corresponding to octahydrocarbazole (II) been obtained.

(III.)   (IV.)

(V.) $CH_2 \!<\! {}^{CH_2}_{CH_2}$
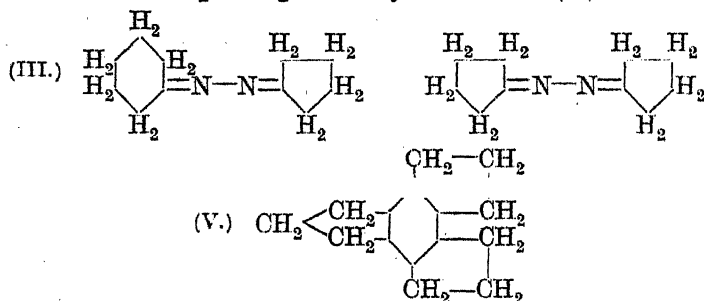
The decomposition of *cyclo*pentylideneazine with hydrogen chloride resulted in the formation of a hydrocarbon (m. p. 97°) of the empirical formula C_5H_6, and it was suggested to us by Prof. Robinson that this unexpected product of the removal of hydrazine from the azine might be tri*cyclo*trimethylenebenzene (V). Such proved to be the case, for the substance is identical with a specimen (m. p. 96—97°) of this hydrocarbon which we obtained by Wallach's method

(*Ber.*, 1897, **30**, 1094) from *cyclo*pentanone by treatment with hydrogen chloride.

The formation of octahydrocarbazole from *cyclo*hexylideneazine is clearly a change exactly analogous to the conversion of phenylbenzylketazine into tetraphenylpyrrole (VIII) (Robinson and Robinson, J., 1918, **113**, 639), but the properties of the derivatives of our octahydrocarbazole are very different from those of the substances to which von Braun and Ritter (*Ber.*, 1922, **55**, 3792) have assigned identical structures. Quite recently (*Ber.*, 1925, **58**, 389) von Braun and Bayer suggested that our octahydrocarbazole has the structure represented by (VI) and they maintain that the fact that it can be easily methylated and ethylated and that the products yield methiodides is inconsistent with the behaviour of pyrrole derivatives. Quite apart from the difficulty of explaining the formation of structure (VI) from *cyclo*hexylideneazine by the removal of ammonia, we cannot agree with the arguments von Braun and Bayer bring forward against our view that formula (II) represents our octahydrocarbazole. It is well known that tetra-alkylated pyrroles exhibit properties which differ in many ways from those of pyrrole and its other derivatives. It is clear that formula (II) represents our octahydrocarbazole as being analogous in constitution to a tetra-alkylated pyrrole such as tetramethylpyrrole (VII) and we find that the two substances have in fact many properties in common.

$$\text{(VI.)} \qquad \text{(VII.)} \qquad \text{(VIII.)}$$
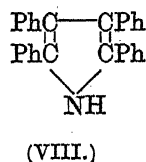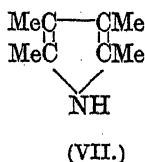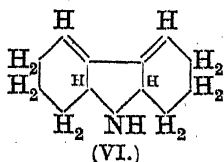
We have prepared tetramethylpyrrole and have confirmed the strongly basic character observed by Fischer and Bartholomäus (*Z. physiol. Chem.*, 1912, **80**, 6) and, although, owing to its instability in air, we have not been able to obtain a pure sample of the methyl derivative, there can be no doubt that tetramethylpyrrole reacts energetically with methyl iodide. The alkyl derivatives of our octahydrocarbazole are also unstable on exposure to air, but less so than the derivatives of tetramethylpyrrole appear to be. We consider, therefore, that the properties of our octahydrocarbazole are those which would be expected in a substance of structure (II) and until very definite evidence in support of such a view is forthcoming, it is clearly unjustifiable to assume that the removal of ammonia from *cyclo*hexylideneazine proceeds in a manner so abnormal as to give rise to a substance of constitution (VI).

The introduction of methyl groups into the nucleus of pyrrole evidently much enhances the basic nature of this substance and it seemed probable that the corresponding introduction of phenyl groups should have the opposite effect, that is to say, would confer acid properties on the $>NH$ group. The examination of the properties of tetraphenylpyrrole (VIII) bears out this view, since this substance is insoluble in dilute acids, does not combine with methyl iodide, and crystallises unchanged from methyl sulphate. On the other hand, the acidic properties of the substance are evidenced by the fact that it yields a methyl derivative when it is treated with methyl sulphate in the presence of potassium hydroxide, obviously because of the intermediate formation of the N-potassium derivative (compare Fehrlin, *Ber.*, 1889, **22**, 555). It is interesting that this methyl derivative crystallises unchanged from methyl sulphate.

The action of hydrogen chloride on *cyclo*hexylidene*cyclo*pentylideneazine (III) was investigated under a variety of conditions, but in all cases resinous products were obtained from which nothing crystalline could be isolated.

EXPERIMENTAL.

*cyclo*Pentylideneazine.—*cyclo*Pentanone (45 g.), dissolved in alcohol (120 c.c.), was mixed with hydrazine hydrate (16 g.), the solution boiled on the steam-bath for 15 minutes and then allowed to stand for several hours. The alcohol was removed by distillation, the residue poured into water, and the solution saturated with salt. The oil was extracted with ether, dried over potassium carbonate, the solvent removed, and the product distilled under reduced pressure, when *cyclo*pentylideneazine was collected as a pale yellow liquid, b. p. 130—132°/22 mm. It solidifies on keeping and melts at 25° (Found : N, 17·0. $C_{10}H_{16}N_2$ requires N, 17·1%).

A solution of *cyclo*pentylideneazine (20 g.) in tetrahydronaphthalene (80 c.c.) was dropped gradually into a small quantity of dry tetrahydronaphthalene, maintained at 180°, through which a stream of dry hydrogen chloride was passed continuously. The solvent was removed in steam, the residue made alkaline with sodium carbonate, and the product extracted with ether. The solution was dried over potassium carbonate, the solvent removed, and the almost black residue was distilled under reduced pressure, when a small quantity of an oil, b. p. 180—185°/30 mm., was collected. This solidified, on cooling, and was recrystallised from alcohol, from which tri*cyclo*trimethylenebenzene separated in long, colourless needles, m. p. 97° (Found : C, 90·8; H, 9·1. Calc. for $C_{15}H_{18}$, C, 90·9; H, 9·1%). A specimen was prepared by the method described by Wallach (*loc. cit.*) and a mixture of the two melted at 97°.

1-*Methyltetraphenylpyrrole.*—Tetraphenylpyrrole (5 g.) was dissolved in acetone (50 c.c.) and treated with methyl sulphate (15 c.c.) and potassium hydroxide (30 g. in saturated aqueous solution) alternately in successive small quantities, during the course of an hour, with continuous shaking. The mixture was diluted with water and the product recrystallised from acetone, from which pure 1-*methyltetraphenylpyrrole* (3·1 g.) was obtained in colourless plates, m. p. 210° (Found : C, 90·5; H, 6·1. $C_{29}H_{23}N$ requires C, 90·4; H, 6·0%).

1-Methyltetraphenylpyrrole is insoluble in dilute acids and can be crystallised unchanged from hot methyl sulphate.

cyclo*Hexylidenecyclopentylideneazine.*—Hydrazine hydrate (35 g.) was dissolved in alcohol (100 c.c.) and treated gradually with cyclohexanone (50 g.) with continuous shaking. The mixture was boiled for 5 hours, the alcohol removed, and the residue distilled under reduced pressure. A fraction (11 g.), b. p. 105—110°/22 mm., was collected consisting of cyclohexanonehydrazone (compare Mailhe, *Compt. rend.*, 1922, **174**, 465); the main product of the reaction being cyclohexylideneazine, b. p. 153°/22 mm. A mixture of the cyclohexanonehydrazone with cyclopentanone (8·5 g.) was heated on the steam-bath for an hour, and the product dissolved in ether and dried with potassium carbonate. After removal of the solvent, a fraction was obtained, b. p. 140—145°/12 mm. This proved to be cyclo*hexylidenecyclopentylideneazine*, but the yield was not good (Found : N, 15·5. $C_{11}H_{18}N_2$ requires N, 15·7%).

CLVIII.—*The Additive Formation of Four-membered Rings. Part VII. The Synthesis and Division of Some Dimethylene-*1 : 3-*oxaimines.*

By CHRISTOPHER KELK INGOLD.

ATTENTION has been directed in previous parts of this series to reversible additive ring formation involving a double equilibrium of the type

$$A\underset{B}{\overset{C}{\underset{|}{|}}} + \overset{C}{\underset{D}{|}} \rightleftharpoons \overset{A-C}{\underset{B-D}{|\quad|}} \rightleftharpoons \overset{A=C}{\underset{B=D}{+}} \quad \cdot\quad\cdot\quad\cdot\quad (i)$$
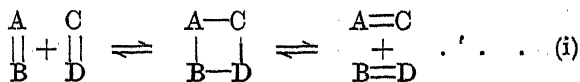
When the intermediate cycloid is stable, as in the case of the ring systems (I) and (II), only a part of the equilibrated system represented by equation (i) can usually be realised.   On the other hand, if the ring is unstable, and fulfils certain other conditions, evidence of the complete balanced action may be obtained.   The rings (III) and (IV) fulfil the necessary conditions :

$$
\begin{array}{cccc}
\underset{(stable)}{\underbrace{\begin{array}{c} \text{C—C} \\ \text{C—C} \end{array} \text{(I.)} \quad \begin{array}{c} \text{C—N} \\ \text{C—O} \end{array} \text{(II.)}}} & & \underset{(unstable)}{\underbrace{\begin{array}{c} \text{C—N} \\ \text{N—C} \end{array} \text{(III.)} \quad \begin{array}{c} \text{C—N} \\ \text{O—C} \end{array} \text{(IV.)}}}
\end{array}
$$
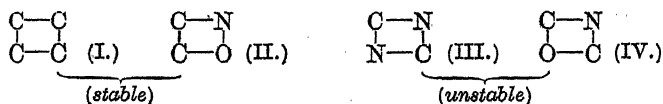
Equilibria dependent on the formation and division of rings of type III were discussed in Part I (Ingold and Piggott, J., 1922, **121**, 2793), and similar equilibria dependent on type IV are now described.

Rings of this type are produced from carbonyl compounds and azomethines, and their division in the two possible directions may give rise to double-bonded products of the same two classes :

$$
\underset{\text{(V.)}}{\text{XYC}:\text{NZ}} + \underset{\text{(VI.)}}{\text{PQC}:\text{O}} \rightleftharpoons \underset{\text{O—CPQ}}{\overset{\text{XYC—NZ}}{}} \rightleftharpoons \underset{\text{(VII.)}}{\text{XYC}:\text{O}} + \underset{\text{(VIII.)}}{\text{PQC}:\text{NZ}}
$$
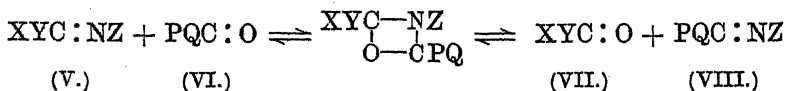
This reaction can be determined completely in either direction in favour of an insoluble participant; thus, if (VIII) is insoluble in some solvent, such as ethyl acetate, it will, in a short time, be quantitatively deposited from an ethyl acetate solution of (V) and (VI), whilst the mother-liquor will yield (VII) on evaporation (see Section B).   In a solvent, however, in which all the participants in the balanced action are readily soluble an equilibrium is attained which can be approached from either end (see Section A).

In some of the cases formerly examined (Part I, *loc. cit.*), the isolation of the extremely unstable intermediate cycloids (type III) was achieved, but in the present experiments cycloids of type (IV) could not be isolated, such rings being, on the whole, apparently even less stable than those of type (III).   In connexion with this difference of stability it is of interest that the union of azomethines and carbimides, which might be expected to yield a ring either of type (III) or of type (IV), actually gives type (III) alone, moderately stable compounds of this class having been obtained by Senior and Shepherd (J., 1909, **95**, 504) and by Hale and Lange (*J. Amer. Chem. Soc.*, 1919, **41**, 384) :

$$
\begin{array}{ccc}
>\text{C}\!\!\equiv\!\!\text{N—} & & >\text{C—N—} \\
+ & \rightarrow & \\
\text{RN}\!\!\equiv\!\!\text{CO} & & \text{RN—C}:\text{O} \\
& & \text{(formed)}
\end{array}
\qquad
\begin{array}{ccc}
>\text{C}\!\!\equiv\!\!\text{N—} & & >\text{C—N—} \\
+ & \rightarrow & \\
\text{O}\!\!\equiv\!\!\text{C}\!:\!\text{NR} & & \text{O—C}:\text{NR} \\
& & \text{(not formed)}
\end{array}
$$
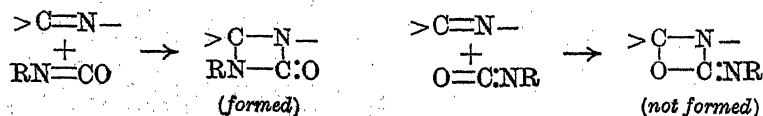
It is also noteworthy that the dimethylene-1 : 3-oxaimine rings (type IV), in which the polarities may be said to be concordant, are so unstable, whereas the "isomeric" dimethylene-1 : 2-oxaimine rings (type II), in which the polarities are discordant, or, at least, less concordant, are quite the most stable four-membered heterocyclic rings which have been produced up to the present time (Ingold and Weaver, J., 1924, **125**, 1456) * :

$$+\overset{|}{C}\text{—}\overset{|}{N}\text{—} \qquad\qquad +\overset{|}{C}\text{—}\overset{|}{N}\text{—}$$
$$-\overset{|}{O}\text{—}\overset{|}{C}+ \qquad\qquad +\overset{|}{C}\text{—}\overset{|}{O}\text{—}$$

    (unstable)   *(stable)*
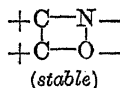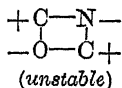
EXPERIMENTAL.

The aldehydes and azomethines produced in the reactions described in Section A were each identified by comparison and by the m. p. of a mixture with an authentic specimen.

(*A*) *Additive Reactions between Carbonyl Compounds and Azomethines Leading to Equilibria which can be Approached from Both Sides.*

(i) *The Reaction* : $(p)NO_2 \cdot C_6H_4 \cdot CHO +$

    $(m)NO_2 \cdot C_6H_4 \cdot CH\mathord{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p) \rightleftharpoons$ cycloid $\rightleftharpoons$

$(p)NO_2 \cdot C_6H_4 \cdot CH\mathord{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p) + (m)NO_2 \cdot C_6H_4 \cdot CHO.$—

(a) *Formation of p-nitrobenzylidene-p-nitrobenzylamine and m-nitrobenzaldehyde from p-nitrobenzaldehyde and m-nitrobenzylidene-p-nitrobenzylamine.* Equimolecular quantities of *p*-nitrobenzaldehyde and *m*-nitrobenzylidene-*p*-nitrobenzylamine were mixed in solution in either ethyl acetate, chloroform or absolute alcohol. After some days, the solution was concentrated in a vacuum and seeded with p-*nitrobenzylidene*-p-*nitrobenzylamine*, with consequent deposition of a considerable quantity of this substance, which was crystallised from benzene and identified by analysis (Found : C, 58·9; H, 3·9. $C_{14}H_{11}O_4N_3$ requires C, 58·9; H, 3·9%) and by direct comparison with a specimen prepared from *p*-nitrobenzaldehyde and *p*-nitrobenzylamine. The mother-liquor was concentrated to a small bulk and the crystallisation of *p*-nitrobenzaldehyde and *m*-nitrobenzylidene-*p*-nitrobenzylamine induced by seeding. The ultimate residues were dissolved in 80% alcohol and extracted with successive quantities of benzene in the hope of isolating the cycloid. This was not obtained, but the earlier extracts yielded fairly pure *m*-nitrobenzaldehyde.

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* A difference in the same sense, although less marked, exists between the dimethylene-1 : 2- and dimethylene-1 : 3-di-imines (this vol., p. 378) :

$$+\overset{|}{C}\text{—}\overset{|}{N}\text{–} \qquad\qquad +\overset{|}{C}\text{—}\overset{|}{N}\text{–}$$
$$-\overset{|}{N}\text{—}\overset{|}{C}+ \qquad\qquad +\overset{|}{C}\text{—}\overset{|}{N}\text{–}$$

    (unstable)   (rather stable)
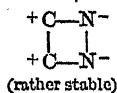
(b) *Formation of* p-*nitrobenzaldehyde and* m-*nitrobenzylidene-*p-*nitrobenzylamine from* p-*nitrobenzylidene-*p-*nitrobenzylamine and* m-*nitrobenzaldehyde.* Solutions of equimolecular quantities of m-nitrobenzaldehyde and p-nitrobenzylidene-p-nitrobenzylamine were mixed as before, and, after allowing time for equilibration, the solution was evaporated at a low temperature and the excess of p-nitrobenzylidene-p-nitrobenzylamine caused to crystallise and removed. The filtrate was concentrated to small bulk, and crops of m-nitrobenzylidene-p-nitrobenzylamine and of p-nitrobenzaldehyde, each more or less contaminated with p-nitrobenzylidene-p-nitrobenzylamine, were obtained by appropriate seeding. The aldehyde was purified by crystallisation from ethyl acetate, and the azomethine by many crystallisations from benzene. (For the azomethine : Found, C, 58·4; H, 4·1. Calc., C, 58·9; H, 3·9%).

(ii) *The Reaction :* (p) $NO_2 \cdot C_6H_4 \cdot CHO$ +
    (m)$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(m)$ ⇌ cycloid ⇌
    (p)$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(m)$ + (m)$NO_2 \cdot C_6H_4 \cdot CHO.$—

(a) *Formation of* m-*nitrobenzylidene-*m-*nitrobenzylamine and* p-*nitrobenzaldehyde from* p-*nitrobenzylidene-*m-*nitrobenzylamine and* m-*nitrobenzaldehyde.* This reaction was carried out like the last, and the p-nitrobenzaldehyde and m-nitrobenzylidene-m-nitrobenzylamine were caused to crystallise by seeding after the solution had been evaporated at a low temperature. Crystallisation of the aldehyde and of the azomethine was favoured by the addition of ethyl acetate and absolute alcohol, respectively, to the concentrated solution. The aldehyde was finally crystallised from ethyl acetate, and the *azomethine* from alcohol and then from benzene (Found : C, 58·7; H, 4·0. $C_{14}H_{11}O_4N_3$ requires C, 58·9; H, 3·9%).

(b) *Formation of* p-*nitrobenzylidene-*m-*nitrobenzylamine and* m-*nitrobenzaldehyde from* m-*nitrobenzylidene-*m-*nitrobenzylamine and* p-*nitrobenzaldehyde.* As much p-nitrobenzaldehyde and m-nitrobenzylidene-m-nitrobenzylamine as possible was crystallised from the equilibrated solution by cautious concentration in the cold, aided by seeding, and the residue was fractionally extracted by the benzene and aqueous alcohol process described above. From the earlier benzene extracts m-nitrobenzaldehyde was readily isolated, and from the later ones a mixture of azomethines, etc., from which p-nitrobenzylidene-m-nitrobenzylamine was obtained by alternate crystallisation from alcohol and benzene.

(B) *Reactions Determined in Favour of an Insoluble Participant.*

(i) *The Reaction :* (p)$NO_2 \cdot C_6H_4 \cdot CHO$ +
    $C_6H_5 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p)$ ⇌ cycloid ⇌
(p)$NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p)$ + $C_6H_5 \cdot CHO.$—This reaction

went practically completely from left to right when p-nitrobenzaldehyde (1·5 g.) and benzylidene-p-nitrobenzylamine (2·4 g.) were dissolved in 5 c.c. of absolute ethyl alcohol. After some hours a crystal of p-nitrobenzylidene-p-nitrobenzylamine was introduced and the mixture kept until deposition of this substance ceased. The liquid was then evaporated to 2 c.c. with the aid of the pump and diluted with 5 c.c. of dry ether; crystals of nearly pure p-nitrobenzylidene-p-nitrobenzylamine were obtained in almost quantitative yield after 1 hour.

The ethereal mother-liquors were evaporated and the liquid residue was treated with an excess of aqueous semicarbazide acetate, when a nearly quantitative yield of benzaldehydesemicarbazone (m. p. 224°, and not 214° as stated in the literature) was obtained. Its identity was confirmed by hydrolysis and subsequent oxidation of the benzaldehyde to benzoic acid.

(ii) *The Reaction* : $(m)NO_2 \cdot C_6H_4 \cdot CHO +$
$C_6H_5 \cdot CH\!:\!N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p) \rightleftharpoons$ cycloid $\rightleftharpoons$
$(m)NO_2 \cdot C_6H_4 \cdot CH\!:\!N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p) + C_6H_5 \cdot CHO$. — m-Nitrobenzaldehyde and benzylidene-p-nitrobenzylamine were allowed to interact as in the last experiment, but in more concentrated solution. The yield of fully purified m-nitrobenzylidene-p-nitrobenzylamine was 80%. Benzaldehyde was isolated from the mother-liquor in the form of its semicarbazone in 90% yield. The products were identified as in the preceding experiment.

(iii) *The Reaction* : $(p)NO_2 \cdot C_6H_4 \cdot CHO +$
$C_6H_5 \cdot CH\!:\!N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(m) \rightleftharpoons$ cycloid $\rightleftharpoons$
$(p)NO_2 \cdot C_6H_4 \cdot CH\!:\!N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(m) + C_6H_5 \cdot CHO$.—This reaction was carried out like the preceding one, but after crystallisation of the p-nitrobenzylidene-m-nitrobenzylamine appeared to have ceased the conversion was rendered quantitative by slow evaporation at the ordinary temperature. The azomethine was isolated and identified like the isomerides previously mentioned, and the benzaldehyde as its semicarbazone, both being obtained in almost theoretical yield.

(iv) *The Reaction* : $(m)NO_2 \cdot C_6H_4 \cdot CHO +$
$C_6H_5 \cdot CH\!:\!N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(m) \rightleftharpoons$ cycloid $\rightleftharpoons$
$(m)NO_2 \cdot C_6H_4 \cdot CH\!:\!N \cdot CH_2 \cdot C_6H_4 \cdot NO_2(m) + C_6H_5 \cdot CHO$.—This reaction was carried out exactly like the preceding one, and the products, benzaldehyde and m-nitrobenzylidene-m-nitrobenzylamine, both obtained in nearly quantitative yield, were isolated and identified in the same way.

THE UNIVERSITY, LEEDS.

CLIX.—*The Explosion of Ammonia with Carbon Monoxide and Oxygen.*

By JOHN WILLIAM BEESON and JAMES RIDDICK PARTINGTON.

IN the experiments of Partington and Prince (J., 1924, **125**, 2018) on the explosion of ammonia with electrolytic gas ($2H_2 + O_2$) the extent of decomposition was found to increase with the proportion of electrolytic gas in the mixture. It was suggested that it would be of interest to repeat the experiments with a mixture of carbon monoxide and oxygen instead of electrolytic gas, since this contains no constituent common to the exploding mixture and the ammonia which is decomposed by the energy liberated in the reaction.

It has now been found that the decomposition of ammonia is, within the limits of experimental error, the same whatever the ammonia content of the combustible mixtures; the mean decomposition, when the initial mixture was at 380 mm. pressure and the steam produced was kept gaseous during the explosion, was 95·3%. The results are, therefore, quite different from those obtained with electrolytic gas. With certain mixtures of high ammonia content, explosion did not occur with a single spark, but ensued when a series of sparks passed through the mixture. Mixtures rather richer in ammonia could not be ignited even after prolonged sparking.

EXPERIMENTAL.

Pure ammonia and oxygen gases were prepared as in the previous research. The carbon monoxide was prepared by dropping cold concentrated sulphuric acid on sodium formate, washed with caustic potash solution, and dried over stick caustic soda and purified phosphorus pentoxide. All the gases were rigorously tested for purity.

The apparatus used was carefully cleaned and dried after each experiment. The gases were collected by the displacement of dry mercury from the vessel L (Fig. 1), from which they could be transferred either to the measuring burette, A, or to the explosion pipette, P. A volume of 300 c.c. of the mixture $2CO + O_2$ was prepared and stored in the bulb S. The constituents of this mixture could be rapidly and completely absorbed by ammoniacal cuprous chloride solution and alkaline sodium hyposulphite solution.

The explosion pipette, P, was immersed in a copper bath, the water at first being at room temperature. In order to eliminate as far as possible the slight barometric and temperature changes during the mixing, the gases were measured out in the pipette in the order : 1 pipette CO; 1 pipette O_2; 1 pipette CO. After the explosion of 50 c.c. of the mixture, and absorption in potash, only about 0·03 c.c.

of unabsorbed gas remained.   The gases were then transferred to the storage bulb, S, protected by the trap, T, and thoroughly mixed. When required, the gas could be forced into the vessel L and thence into the calibrated burette, A, for measurement.   All readings were taken after an upward displacement of the mercury.

The *ammonia* gas, generated from pure materials (Partington and Prince, *loc. cit.*), was introduced through L; the part remaining in L was completely absorbed by dilute sulphuric acid.   The mixture of ammonia, carbon monoxide and oxygen was then transferred to the bulb P, thoroughly mixed by splashing the mercury in the bulb, and heated to 85° in the water-bath.   The volume was such that the bulb was just filled to the mark at a pressure of 380 ± 1 mm. at 85°. The gas was then fired.

FIG. 1.
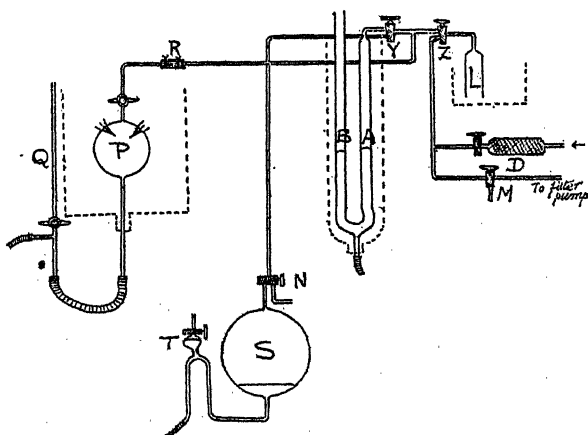
The explosion in the case of mixtures having a low ammonia content was apparently instantaneous, the flame being blue.   Mixtures containing 40·5% or more of ammonia did not fire at the first spark, but only after the mixture had been sparked from 1 second in the case of a mixture of 40·9% of ammonia to 4 or 6 seconds in the case of a mixture containing 46%.   When the reaction occurred after this period of induction, the speed of propagation of the flame from the spark to the walls of the bulb was so slow that it could be followed by the eye.

The gas after the explosion was immediately passed back to the burette.   As it cooled, water was deposited, carrying with it undecomposed ammonia and the carbon dioxide produced in the explosion. It was not possible, therefore, to measure the true volume of the total gaseous products of reaction.   Attempts to liberate the carbon

dioxide by dilute acid were not successful, since the gas formed a highly supersaturated solution. The carbon dioxide was estimated from the difference between the carbon monoxide introduced and that found in the residue, after the carbon dioxide in the gas had been removed by washing with dilute potash solution. Potash (50%) absorbed carbon monoxide to an appreciable extent. The mixture of carbon monoxide, nitrogen and hydrogen was measured over boiled, dilute sulphuric acid (1 : 5), as were all the remaining volumes. The carbon monoxide was then absorbed by three washings of 4 c.c. of ammoniacal cuprous chloride solution. The residue of nitrogen and hydrogen was mixed with a large measured excess of oxygen and exploded in the bulb P. From the results the composition of the gaseous mixture after explosion could be calculated.

The only rubber connexions were the two shown in the figure. These were made with new pressure tubing wired on and cemented to the glass by Faraday's cement. The joint showed no leak over-night with a pressure difference of 50 cm. of mercury (cementing was essential). Errors due to loss in transfer were thus entirely avoided. The error in the burette reading was estimated by experiment at about 1 in 4000. The main source of error was in the absorption in the reagents. No appreciable absorption of carbon monoxide occurred in 1 hour with 23 c.c. of the gas in contact with 10 c.c. of 10% potash solution. The carbon monoxide figures would thus tend to be slightly high owing to solution of the nitrogen and hydrogen in the cuprous chloride solution. A relatively large volume (12 c.c.) of the latter was required for complete absorption. The ammonia left in the gas was removed by two washings each with 4 c.c. of dilute sulphuric acid. The error due to solution of hydrogen in the reagents would be entirely eliminated in the calculation of the percentage decomposition of the ammonia, but the solution of the nitrogen is a possible source of slight error. On the whole, the individual values of gas concentrations in the exploded mixture can probably be relied upon to about 1%. The values of the gas concentrations before explosion are probably accurate to well within 0.5%.

The results of the experiments are given in Table I. In experiments 8 and 15 periods of induction were observed. The volumes of carbon monoxide and hydrogen were directly determined in the exploded mixture. The volumes of the remaining constituents were calculated.

In Table II the relative volumes of the products of explosion in the mixture are calculated, together with the values of
$$K = [CO][H_2O]/[CO_2][H_2],$$
the constant of the water-gas equilibrium. A comparison of the

TABLE I.

No. of Expt.	Composition of original gas.			Volumes of products of explosion in c.c.							% NH₃ decomp.
	% NH₃.	% CO.	% O₂.	CO.	H₂.	CO₂.	N₂.	H₂O.	NH₃.	Total	
14	27·61	48·25	24·13	9·27	5·00	7·99	4·76	9·27	0·35	36·64	96·4
13	28·21	47·86	23·93	9·95	4·22	7·04	4·74	9·95	0·54	36·44	94·61
10	30·16	46·56	23·24	9·96	5·31	6·54	5·09	9·96	0·51	37·37	95·26
17	33·61	44·17	22·08	9·23	6·90	5·34	5·37	9·23	0·40	36·47	96·4
11	34·92	43·40	21·69	10·52	6·80	4·42	5·77	10·52	0·48	38·51	96·0
12	37·67	41·54	20·77	10·39	8·12	3·82	6·17	10·39	0·55	39·44	95·7
19	37·6	41·6	20·8	10·19	8·17	4·25	6·12	10·19	0·84	39·76	93·6
7	40·04	39·97	19·99	10·28	10·40	4·19	6·88	10·28	0·73	42·76	95·0
5	40·20	39·85	19·95	10·64	9·72	3·68	6·81	10·64	0·82	42·31	94·3
15	40·88	39·41	19·70	10·40	9·89	4·08	6·76	10·40	1·52	43·05	89·9
8	45·74	36·16	·18·08	9·97	9·69	3·49	6·33	9·97	4·43	43·88	74·3
9	48·0;	34·70	17·36	Gas could not be exploded even on prolonged sparking.	,,	,,	,,	,,	,,	,,	
18	49·3;	33·73	16·89	,,	,,	,,	,,	,,	,,	,,	

TABLE II.

Relative Volumes of Products of Explosion.

= Vols./total vol. of mixture.

Expt.	CO.	H₂.	CO₂.	N₂.	H₂O.	NH₃.	$K = \dfrac{[CO][H_2O]}{[CO_2][H_2]}$.
14	0·253	0·137	0·218	0·130	0·253	0·00957	2·14
13	0·274	0·116	0·193	0·130	0·274	0·0147	3·35
10	0·266	0·142	0·175	0·136	0·266	0·0136	2·85
17	0·253	0·189	0·146	0·147	0·253	0·0109	2·31
11	0·274	0·177	0·115	0·150	0·274	0·0125	3·69
12	0·261	0·206	0·097	0·157	0·261	0·0139	3·41
19	0·256	0·205	0·107	0·154	0·256	0·021	2·99
7	0·240	0·243	0·098	0·160	0·240	0·0170	2·42
5	0·251	0·230	0·087	0·161	0·251	0·0194	3·16

latter with the known values of the constant (Partington and Shilling, *J. Soc. Chem. Ind.*, 1925, **44**, 149T) shows that a water-gas equilibrium is set up as the gases cool after the explosion, the average temperature at which the equilibrium becomes fixed being in the neighbourhood of 1282° C. Calculation shows, as would be expected, that the ammonia equilibrium is not established.

Summary.

1. Mixtures of ammonia gas with $2CO + O_2$ in varying proportions were exploded at an initial temperature of 85° and pressure of 380 mm., so that no steam condensed during the explosion.

2. Mixtures containing more ammonia than corresponds with the ratio $NH_3/(2CO + O_2) = 0.924$ could not be ignited by sparks. All mixtures which could be ignited showed approximately the same decomposition of the ammonia, *viz.*, 95·3%. With some mixtures richer in ammonia than 40·5% a period of induction was observed.

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CLX.—*Aromatic Esters of Acylecgonines.*

By WILLIAM HERBERT GRAY.

NATURALLY-OCCURRING cocaine has served in several ways as a starting point in the search for the ideal local anæsthetic of low toxicity. The characteristics of its structure essential to the development of pronounced anæsthetic action are now recognised to be the amino- and acylated alcohol groups (I). A large variety of aminoalkyl esters, not containing the bridged ring of cocaine, has been synthesised and some of these, including "novocaine," "stovaine," and "β-eucaine," are ·in common use. In them, however, the power of penetrating mucous membrane possessed by cocaine, which, for example, renders it so valuable in causing corneal anæsthesia, is but feebly developed.

In another scheme, the tropane skeleton has been retained and the effect of variation of the ester groups investigated. Substitution of any other acyl radical for the benzoyl group very greatly diminishes the anæsthetic action, but the *O*-methyl group may give place to higher aliphatic homologues, yielding substances with the typical properties of cocaine (Merck, *Ber.*, 1885, **18**, 2954; Novy, *Amer. Chem. J.*, 1888, **10**, 147):

(I.) $\begin{array}{c} \text{CH}_2\text{-CH---CH·CO}_2\text{Me} \\ | \quad\text{NMe }\text{CH·OBz} \\ \text{CH}_2\text{-CH---CH}_2 \end{array}$ $\begin{array}{c} \text{CH}_2\text{-CH---CH·CO}_2\text{CH}_2\text{Ph} \\ | \quad\text{NMe }\text{CH·OBz} \\ \text{CH}_2\text{-CH---CH}_2 \end{array}$ (II.)

$\begin{array}{c} \text{CH}_2\text{-CH---CH·CO}_2\text{CHMePh} \\ | \quad\text{NMe }\text{CH·OBz} \\ \text{CH}_2\text{-CH---CH}_2 \end{array}$ (III.)
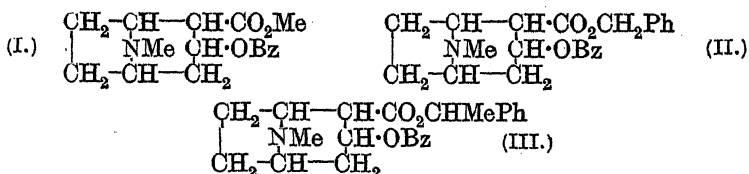
It seemed to be of particular interest to replace this methyl group by aromatic alcohol residues, aliphatic groups alone having been hitherto used. The simple aromatic alcohols have been shown to act as local anæsthetics (Macht, *J. Pharmacol.*, 1918, **12**, 263; Hirschfelder, Lundholm, and Norrgard, *ibid.*, 1920, **15**, 261). *Benzoyl*-1-*ecgonine* esters of *benzyl* (II), p-*nitrobenzyl*, o-*hydroxybenzyl*, α-*phenylethyl*, β-*phenylethyl*, and γ-*phenyl*-n-*propyl alcohols*, together with the *benzyl* and β-*phenylethyl* esters of *benzoyl*-d-ψ-*ecgonine*, have now been prepared, and, with the benzyl group in this position, the corresponding *tropoyl*, *salicyloyl*, and *hydroxytoluoyl* esters of *benzyl*-1-*ecgonine*. It was not found possible to esterify ecgonine with benzyl alcohol by the ordinary Fischer-Speier procedure, nor to effect an interchange of ester groups by heating cocaine with benzyl alcohol. Treatment of the sodium salt of benzoylecgonine with the appropriate aralkyl chloride was, however, found to give the desired esters in good yield. With two exceptions, these were obtained as oils at the ordinary temperature; their picrates, but not the other salts, also have unusually low melting points. The salts of the d-ψ-ecgonine derivatives show the comparatively sparing solubility in water which characterises d-ψ-ecgonine derivatives in general. Attempts to prepare the simplest representative, phenylbenzoyl-l-ecgonine, were unsuccessful.

The anæsthetic and toxic effects of these substances have been studied by Dr. J. Trevan and Miss E. M. Boock, of the Wellcome Physiological Research Laboratories, to whom the author desires to tender his warmest thanks. Their results are here briefly summarised and will be published in full at a later date. All the new esters, with three exceptions, are more active anæsthetics than cocaine, as tested on the cornea of the rabbit. The minimum effective concentration of the best of these, benzylbenzoyl-d-ψ-ecgonine, is one-fourth that of cocaine. Five are better anæsthetics than cocaine as tested by subcutaneous injection; of these the best, β-phenylethylbenzoyl-d-ψ-ecgonine and α-phenylethylbenzoyl-l-ecgonine, are active in one-eighth the concentration required by cocaine. The toxicity of the substances just mentioned, as determined by intravenous injection into mice, is considerably less than that of cocaine in the case of the first, and only slightly greater than that of cocaine in the second and third. Apart from these,

a rough parallelism is observable between degree of anæsthetic action and toxicity. It has been stated that the function of the alkyl ester group is merely the removal of acidic character, the nature of the alcohol used being of no consequence (Fränkel, "Die Arzneimittel Synthese," Berlin, 1921, pp. 335, 353). The results tabulated below show, on the contrary, that changes in this group may exert a notable influence on pharmacological action. Three compounds belonging to a homologous series, viz., benzyl, β-phenyl-ethyl, and γ-phenyl-n-propyl esters of benzoyl-l-ecgonine, were prepared, and it was found that the anæsthetic effect falls off suddenly after the second member of the series is passed. In other instances in which pharmacological effect has been correlated with length of side-chain, for example, the sympathomimetic action of the phenylalkylamines (Barger and Dale, J. Physiol., 1910, 41, 19) and the disinfectant action of the alkyl hydrocupreines (Schaeffer, Biochem. Z., 1917, 83, 269), a similar effect has been noticed. The benzoyl-d-ψ-ecgonine esters were more active than their isomerides, thus falling into line with the corresponding d-ψ-cocaine (compare Gottlieb, Arch. exper. Path. Pharmakol., 1923, 97, 113). The ester of secondary phenylethyl alcohol (III) was more active than that of the corresponding primary alcohol and slightly less toxic. It may be noted that the three esters with acyl groups other than benzoyl provide no exception to the rule indicated in the second paragraph, although the salicyloyl compound is a more active surface anæsthetic than cocaine.

TABLE.

The substances are arranged in order of decreasing action on the cornea, in percentage strength of aqueous solutions of a salt. Toxicities are expressed in mg./kilo of body-weight required to kill 50% of the mice used.

Name.	Minimum effective concentration.		Average lethal dose.
	Corneal.	Subcutaneous.	
Benzylbenzoyl-d-ψ-ecgonine *	0·05—0·025	0·01 —0·005	39
β-Phenylethylbenzoyl-d-ψ-ecgonine	0·1 —0·05	0·005—0·0025	18
α-Phenylethylbenzoyl-l-ecgonine	0·1 —0·05	0·005—0·0025	18
β-Phenylethylbenzoyl-l-ecgonine	0·1 —0·05	0·01 —0·005	16·5
Benzylbenzoyl-l-ecgonine	0·1 —0·05	0·01 —0·005	33
Benzylsalicyloyl-l-ecgonine	0·1 —0·05	0·1 —0·05	ca. 90
γ-Phenyl-n-propylbenzoyl-l-ecgonine	0·1	0·1 —0·05	45·5
o-Hydroxybenzylbenzoyl-l-ecgonine	>0·1	>0·1	50
Methylbenzoyl-l-ecgonine (cocaine)	0·2 —0·1	0·04	25
Benzyl-2-hydroxy-3-methylbenzoyl-l-ecgonine	>0·2	0·2 —0·1	ca. 50
p-Nitrobenzylbenzoyl-l-ecgonine	>0·5	0·1 —0·05	ca. 50
Benzyltropoyl-l-ecgonine	1·0 —0·5	0·05—0·025	ca. 40

* Subsequent to the completion of this work a paper has appeared (Poulsson and Wiedemann, Arch. exper. Path. Pharmakol., 1925, 105, 58) in which the preparation of a benzylbenzoylecgonine is described; the melting point of the hydrochloride is, however, considerably lower than that of ours.

EXPERIMENTAL.

The esters of benzoyl-*l*-ecgonine were prepared, in general, by heating an intimate mixture of benzoyl-*l*-ecgonine (1 mol.), powdered sodium hydroxide (1 mol.), excess of appropriate aralkyl chloride (3 mols.), and a small quantity of pyridine. The pasty reaction mixture was stirred frequently and heated for 7 hours at suitable temperatures ranging from 90° to 120°. The cooled product was treated with dilute acid and freed from aralkyl chloride by agitation with ether; after saturation with sodium bicarbonate, the new base was extracted with ether and purified by means of a salt.

The esters of the other acylecgonines were more conveniently made by the converse procedure, as follows. The hydrochloride of *l*-ecgonine or *d*-ψ-ecgonine was first treated in the manner just described with aralkyl chloride and sodium hydroxide (2 mols.), which converted it into the corresponding alkylecgonine, which was soluble in organic solvents. This base was then acylated by the appropriate reagent, for instance, benzoic anhydride in benzene solution.

*Benzylbenzoyl-*1*-ecgonine.*—Benzoylecgonine (12 g.), powdered sodium hydroxide (1·33 g.), benzyl chloride (13·3 c.c.), and pyridine (1·7 c.c.) were thoroughly mixed and treated as above, yielding 10·6 g. of base as a thick oil with a tropine-like odour. It could not be crystallised and was purified for analysis by regeneration from the hydrochloride (Found: C, 73·1; H, 6·9; N, 3·6. $C_{23}H_{25}O_4N$ requires C, 72·8; H, 6·6; N, 3·7%). The *hydrochloride* crystallises from dry acetone in lustrous, six-sided leaflets, m. p. 171° (corr.), soluble in its own weight of water, readily soluble in alcohol, and sparingly soluble in acetone; $[\alpha]_D$–18·62° in 2% aqueous solution. The dilute aqueous solution causes persistent numbness when placed on the tongue. The yield of the pure salt was 51% of the benzoylecgonine taken (Found: Cl, 8·5. $C_{23}H_{25}O_4N,HCl$ requires Cl, 8·5%). The *nitrate* crystallises from acetone in fine needles, m. p. 163° (corr.; decomp.) (Found. C, 61·9; H, 5·9; N, 6·4. $C_{23}H_{25}O_4N,HNO_3$ requires C, 62·4; H, 5·9; N, 6·3%). The *hydrogen sulphate* is insoluble in acetone. It crystallises from alcohol in clusters of rectangular plates, m. p. 206—208° (corr.). (Found: S, 6·55. $C_{23}H_{25}O_4N,H_2SO_4$ requires S, 6·7%). The *chloroaurate* crystallises from boiling methyl alcohol, in which it is sparingly soluble, in large, glistening plates, m. p. 111° (corr.), insoluble in water, ethyl alcohol, or petroleum, readily soluble in chloroform or acetone. (Found: Au, 27·8. $C_{23}H_{25}O_4N,HCl,AuCl_3$ requires Au, 27·4%). The *chloroplatinate* is precipitated from aqueous solutions in minute needles, m. p. 210° (corr.), with two molecules of water of crystallisation, which it loses at 60° in a vacuum.

The dried substance melts at 211° (corr.) [Found : loss at 60°, 3·4. $(C_{23}H_{25}O_4N,HCl)_2,PtCl_4,2H_2O$ requires H_2O, 3·0%. Found, in the dried substance : Pt, 16·7. $(C_{23}H_{25}O_4N,HCl)_2,PtCl_4$ requires Pt, 16·7%]. The *picrate*, precipitated from aqueous solutions, separates from hot absolute alcohol as an oil, slowly changing on standing into clumps of needles, m. p. 80° [Found : N, 9·15. $C_{23}H_{25}O_4N,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 9·2%.]

p-*Nitrobenzylbenzoyl-l-ecgonine.*—As the esterification appeared to proceed with unusual readiness in this case, the action of p-nitrobenzyl chloride on cocaine was tried under similar conditions, to ascertain if interchange of ester groups would take place. Considerable tar formation occurred, however, and the only product isolated was unchanged cocaine.

Benzoylecgonine (12 g.), sodium hydroxide (1·3 g.), p-nitrobenzyl chloride (20 g.), and pyridine (1·3 c.c.) yielded by the standard procedure 12 g. of base, which did not crystallise, and was purified by means of its hydrochloride (Found : C, 64·9; H, 5·8; N, 6·6. $C_{23}H_{24}O_6N_2$ requires C, 65·1; H, 5·7; N, 6·6%). The crude crystalline *hydrochloride*, after being washed with cold acetone to remove a coloured impurity, crystallised from boiling acetone in minute leaflets, m. p. 178·5° (corr.). It is soluble in 40 parts of water at 15°, readily soluble in chloroform, sparingly soluble in alcohol or acetone; $[\alpha]_D + 17{\cdot}98°$ in 2% aqueous solution (Found : Cl, 7·6. $C_{23}H_{24}O_6N_2,HCl$ requires Cl, 7·7%). The *nitrate* was precipitated from a solution of the hydrochloride by dilute nitric acid in fine, silky needles, m. p. 187° (corr.), and was almost insoluble in water (Found : C, 56·4; H, 5·3; N, 8·7. $C_{23}H_{24}O_6N_2,HNO_3$ requires C, 56·7; H, 5·4; N, 8·6%). The *hydrogen sulphate* is prepared similarly, but needed to be recrystallised from alcohol; needles, m. p. 195° (corr.) (Found : S, 6·3. $C_{23}H_{24}O_6N_2,H_2SO_4$ requires S, 6·1%). The *chloroaurate* crystallises from methyl alcohol in well-formed prisms, m. p. 154° (corr.) (Found : Au, 25·8. $C_{23}H_{24}O_6N_2,HCl,AuCl_3$ requires Au, 25·8%). The *chloroplatinate* is practically insoluble in methyl or ethyl alcohol, and crystallises from hot water in glistening, elongated plates, m. p. 204—205° (corr.; decomp.). At 60°, this lost $2\frac{1}{2}H_2O$ and then melted at 210° (corr.) [Found : loss at 60°, 3·6. $(C_{23}H_{24}O_6N_2,HCl)_2,PtCl_4,2\frac{1}{2}H_2O$ requires H_2O, 3·45%. Found, in the dried substance; Pt, 15·6. $(C_{23}H_{24}O_6N_2,HCl)_2,PtCl_4$ requires Pt, 15·5%]. The *picrate* crystallises from alcohol in clusters of fine needles, m. p. 84° (corr.) [Found : N, 10·8. $C_{23}H_{24}O_6N_2,C_6H_2(NO_2)_3{\cdot}OH$ requires N, 10·7%].

Attempts were made to reduce this substance to the corresponding amino-ester; a number of reducing agents were tried, but in no case was the desired product obtained.

o-*Hydroxybenzylbenzoyl*-l-*ecgonine.*—Attempts to prepare o-hydroxybenzyl chloride from saligenin led only to copious tar formation, and the alternative of acting upon saligenin with an acid chloride of ecgonine or benzoylecgonine was not realised; by the action of thionyl chloride on these bases only their hydrochlorides could be isolated. Interchange of ester groups did not occur when saligenin and cocaine were heated together, unchanged cocaine being recovered or resinous products formed according to the temperature employed. The ester was finally obtained by the use of o-*acetoxybenzyl chloride*, the acetyl group being removed without special treatment during the purification process. This substance, the preparation of which does not appear to have been described, was obtained as follows. Monoacetylsaligenin (Hart and Hirschfelder, *J. Amer. Chem. Soc.*, 1921, **43**, 1688) (26·8 g.) was dissolved in an equal volume of diethylaniline and treated with thionyl chloride (14 c.c.). After standing over-night, the mixture was heated at 110—120° for 8½ hours and worked up according to the procedure of Darzens for phenylethyl chloride (*Compt. rend.*, 1911, **152**, 1314). The chloride is a colourless oil with a faint, pleasant smell, b. p. 135°/14 mm. (Found : C, 59·0; H, 5·2. $C_9H_9O_2Cl$ requires C, 58·5; H, 4·9%). For preparation of the ester the fraction collected over 142—150°/20 mm. was used without further purification, 9·6 g. being treated as above with benzoylecgonine (6 g.), sodium hydroxide (0·7 g.), and pyridine (0·15 c.c.), yielding 6 g. of oil, which was purified by conversion into the hydrochloride and treatment of this with ether. Neither the base nor the hydrochloride was obtained crystalline (Found : C, 69·1; H, 6·6; N, 3·6. $C_{23}H_{25}O_5N$ requires C, 69·85; H, 6·4; N, 3·6%). The *picrate* was dried for analysis at 60° in a vacuum [Found : N, 9·2. $C_{23}H_{25}O_5N,C_6H_2(NO_2)_3\cdot OH$ requires N, 9·0%).

β-*Phenylethylbenzoyl*-l-*ecgonine.*—Benzoylecgonine (10·1 g.), sodium hydroxide (1·08 g.), phenylethyl chloride (17·1 c.c.) (Darzens, *loc. cit.*), and pyridine (1·5 c.c.) were heated together at 120°; at a lower temperature, the yield was unsatisfactory. The base crystallised directly on evaporation of the dried ethereal extract, in rosettes of needles, m. p. 100° (corr.) after recrystallisation from alcohol (Found : C, 73·1; H, 7·1; N, 3·7. $C_{24}H_{27}O_4N$ requires C, 73·3; H, 6·9; N, 3·6%). The *hydrochloride* crystallises from dry acetone in elongated, flattened prisms, m. p. 196° (corr.), readily soluble in water or alcohol, sparingly soluble in acetone; $[\alpha]_D$ —39·2° in 2% aqueous solution (Found : Cl, 8·3. $C_{24}H_{27}O_4N,HCl$ requires Cl, 8·25%). The *chloroplatinate* crystallises from methyl alcohol in delicate, six-sided plates, m. p. 216° (corr.) [Found : Pt, 16·4. $(C_{24}H_{27}O_4N,HCl)_2,PtCl_4$ requires Pt, 16·3%]. The *picrate* was precipitated from aqueous solutions as a granular solid, m. p. 66°

(corr.) [Found :   N,   9·0. $C_{24}H_{27}O_4N,C_6H_2(NO_2)_3\cdot OH$ requires N, 9·0%].

α-Phenylethylbenzoyl-l-ecgonine.—Phenylmethylcarbinol, obtained by reduction of acetophenone (Klages and Allendorff, *Ber.*, 1898, **31**, 1003) gave a moderate yield of the corresponding chloride by the thionyl chloride method, but a much better result by treatment with calcium chloride and dry hydrogen chloride (Engler and Bethge, *Ber.*, 1874, **7**, 1127). A temperature above 100° could not be employed in the esterification, hydrogen chloride being evolved and a very poor yield obtained. The reaction proceeded slowly at 100°, heating for several days being required. In this case the product was first treated with acetone, unchanged benzoylecgonine hydrochloride remaining undissolved. 12·8 C.c. of α-chloroethyl-benzene and 7·6 g. of benzoylecgonine yielded in this way 5·0 g. of pure base as an oil (Found : C, 72·95; H, 7·2; N, 3·6. $C_{24}H_{27}O_4N$ requires C, 73·3; H, 6·9; N, 3·6%). The *hydrochloride* is extremely deliquescent; it may be precipitated as a solid by mixing solutions of the base and hydrogen chloride in dry ether, and is readily soluble in acetone. The *hydrobromide* and *nitrate* are also very deliquescent. The *chloroaurate* crystallises from alcohol in clusters of thin plates, m. p. 170° (corr.). It is more readily soluble in organic solvents than the other chloroaurates described in this paper (Found : Au, 26·9. $C_{24}H_{27}O_4N,HCl,AuCl_3$ requires Au, 26·9%).

Phenyl - n - propylbenzoyl - l - ecgonine.—γ-Phenyl-*n*-propyl alcohol was prepared by running a mixture of cinnamyl alcohol and absolute alcohol (1 mol.) on to freshly-cut sodium at 100°. Phenylpropyl chloride (10·3 g.), prepared from this by the thionyl chloride method (see above), benzoylecgonine (5·54 g.), sodium hydroxide (0·59 g.), and pyridine (0·8 c.c.) yielded, at 120°, 5·9 g. of crude base. Impurities were removed by extracting the aqueous hydrochloride solution with ether, and 5·6 g. of pure base recovered as an oil (Found : C, 73·5; H, 7·25; N, 3·4. $C_{25}H_{29}O_4N$ requires C, 73·65; H, 7·2; N, 3·4%). The *hydrochloride* was not obtained crystalline.

Benzyltropoyl-l-ecgonine.—Treatment of ecgonine hydrochloride with acetyltropyl chloride (compare the partial synthesis of atropine by Wolffenstein and Mamlock, *Ber.*, 1908, **41**, 723), followed by esterification of the resulting product, gave a small yield of base soluble in ether, but a much better result was obtained by first benzylating the ecgonine, and treating the base so obtained with acetyltropyl chloride. Ecgonine hydrochloride (8·8 g.) and benzyl chloride (16 c.c.) gave by the standard procedure 7·7 g. of ether-soluble base, which, without further purification, was heated with the acetylchloride from 8 g. of tropic acid (Wolffenstein and Mamlock, *loc. cit.*). The tough solid obtained was purified by repeated

solution in acetone and precipitation with ether, and yielded 6·2 g. of base as an uncrystallisable oil (Found: C, 71·1; H, 7·1; N, 3·4. $C_{25}H_{29}O_5N$ requires C, 70·9; H, 6·9; N, 3·3%). The hydrochloride also was an oil, soluble with difficulty in water; for the preparation of the salts and for physiological testing, a solution of the lactate was used. The *chloroaurate* formed small needles, m. p. 90° (corr.) (Found : Au, 25·2. $C_{25}H_{29}O_5N,HCl,AuCl_3$ requires Au, 25·8%). The *picrate* is a granular solid, m. p. 65° (corr.) [Found : N = 8·7. $C_{25}H_{29}O_5N,C_6H_2(NO_2)_3 \cdot OH$ requires N, 8·6%].

Benzyl-o-hydroxybenzoyl-l-ecgonine.—Sodium salicylate (12·8 g.) was converted into salicyloyl chloride (Kopetschni and Karczag, D.R.-P. 262883) and heated at 100° under reduced pressure with benzylecgonine (6·6 g.), prepared as described above, for 2 hours. The product was dissolved in water and purified by agitation with ether, 5·3 g. of base being obtained. Neither this nor the hydrochloride could be crystallised and the base was purified through the *picrate*, small columns, m. p. 67° (corr.) [Found : N, 8·9. $C_{23}H_{25}O_5N,C_6H_2(NO_2)_3 \cdot OH$ requires N, 9·0%. Found, on the base : C, 70·3; H, 6·5; N, 3·5. $C_{23}H_{25}O_5N$ requires C, 69·85; H, 6·4; N, 3·5%].

Benzyl-2-hydroxy-3-methylbenzoyl-1-ecgonine.—This and the following base were prepared from sodium *o*- and *m*-hydroxytoluates respectively in the same way as benzyl-*o*-hydroxybenzoyl-*l*-ecgonine. They were not obtained crystalline, and were purified by means of their picrates (Found : C, 70·3; H, 6·8; N, 3·5. $C_{24}H_{27}O_5N$ requires C, 70·4; H, 6·65; N, 3·4%). The *picrate* is a granular solid, m. p. 67° (corr.) [Found : N, 8·8. $C_{24}H_{27}O_5N,C_6H_2(NO_2)_3 \cdot OH$ requires N, 8·8%].

Benzyl-2-hydroxy-4-methylbenzoyl-1-ecgonine (Found : C, 70·3; H, 6·8; N, 3·4. $C_{24}H_{27}O_5N$ requires C, 70·4; H, 6·65; N, 3·4%). The *picrate* is a granular solid, m. p. 70° (corr.) [Found : N, 8·8. $C_{24}H_{27}O_5N,C_6H_2(NO_2)_3 \cdot OH$ requires N, 8·8%].

Benzylbenzoyl-d-ψ-ecgonine.—Poor yields of benzoyl-*d*-ψ-ecgonine were obtained by the procedure of D. R.-P. 55338, or when *d*-ψ-ecgonine was treated with benzoyl chloride. *d*-ψ-Ecgonine hydrochloride (3·2 g.), benzyl chloride (6 c.c), sodium hydroxide (1·2 g.), and pyridine (0·6 c.c.) reacted vigorously at 150° and yielded, after heating for ½ hour, 2·8 g. of benzyl-*d*-ψ-ecgonine as an oil, soluble in organic solvents. This base (3·6 g.) was dissolved in an equal weight of dry benzene and heated under reflux with benzoic anhydride (9·2 g.) for 6 hours, 35 c.c. of ether were then added, and the filtered solution was shaken with 30 c.c. of 7% hydrochloric acid. A copious separation of glistening platelets, m. p. 211° (corr.), of benzylbenzoyl-*d*-ψ-ecgonine hydrochloride occurred (yield 2·53 g.),

from which the base was obtained as a colourless oil by agitation with sodium bicarbonate solution and ether (Found : C, 72·6; H, 7·0; N, 3·7. $C_{23}H_{25}O_4N$ requires C, 72·8; H, 6·6; N, 3·7%). The *hydrochloride*, obtained as already described, was washed free from traces of colouring matter by cold dry acetone, in which it is almost insoluble; m. p. 213° (corr.). It is readily soluble in hot water, but very sparingly soluble at 20° (Found : Cl, 8·55. $C_{23}H_{25}O_4N,HCl$ requires Cl, 8·5%). The *nitrate* crystallises from dilute alcohol in small, square plates, m. p. 168° (corr.) (Found : C, 62·4; H, 6·2; N, 6·4. $C_{23}H_{25}O_4N,HNO_3$ requires C, 62·4; H, 5·9; N, 6·3%). The neutral *tartrate* crystallises from water, in which it is moderately soluble, in fine needles, m. p. 155° (corr.). It is readily soluble in alcohol. The *mucate* forms felted needles, m. p. 142—143° (corr.), very sparingly soluble in cold water. The *picrate* is precipitated from aqueous solutions as a granular solid, m. p. 80° (corr.) [Found : N, 9·2. $C_{23}H_{25}O_4N,C_6H_2(NO_2)_3 \cdot OH$ requires N, 9·2 %].

β-*Phenylethylbenzoyl*-d-ψ-*ecgonine* was prepared in the same way as the preceding ester, but the hydrochloride was more soluble and did not crystallise directly. 5·5 Grams of d-ψ-ecgonine hydrochloride yielded 5·7 g. of base, which, after purification by means of the hydrochloride, crystallised in square plates, m. p. 63° (corr.) (Found : C, 73·3; H, 6·9; N, 3·5. $C_{24}H_{27}O_4N$ requires C, 73·3; H, 6·9; N, 3·6%). The *hydrochloride* crystallises from acetone in silky needles, m. p. 197° (corr.), soluble in 89·6 parts of water at 16°; $[\alpha]_D + 35 \cdot 0°$ in 1% aqueous solution (Found : Cl, 8·35. $C_{24}H_{27}O_4N,HCl$ requires Cl, 8·25%).

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CLXI.—*Strychnine and Brucine. Part III. The Position of the Methoxyl Groups in Brucine.*

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THE first clear evidence that the molecule of brucine contains two methoxyl groups in an aromatic nucleus which are in the ortho- or para-positions to each other was furnished by Leuchs and Geiger

(*Ber.*, 1909, **42**, 3067), who showed that a brucinesulphonic acid is changed by nitric acid to a related quinone and a nitro-quinone by simultaneous oxidation and demethylation with or without nitration. This was followed by numerous similar observations on the part of Leuchs and his co-workers. Thus Leuchs and Weber (*Ber.*, 1909, **42**, 3703) obtained a quinone and corresponding quinol from brucinolone, and Leuchs and Anderson (*Ber.*, 1911, **44**, 2136) prepared bis*apo*methylbrucine itself. On the assumption that brucine is a dimethoxytetrahydroquinoline derivative, Tafel and Moufang (*Annalen*, 1899, **304**, 25) expressed the opinion that one of the methoxyls occupies the position in the benzene ring para to the nitrogen atom, but there is no proof of this and the position occupied by these groups is not indicated by any degradation product of brucine as yet obtained. It occurred to us that, since the brucine–nitric acid reaction is so characteristic, some indirect but nevertheless valuable information might be gleaned from the study of the behaviour with nitric acid of synthetical compounds containing methoxyl groups oriented so as to be typical of the various possibilities which must be considered in the case of brucine. The series which we chose for examination was that of the *N*-acetyl-dimethoxydimethyltetrahydroquinolines (I, II, III, IV), which were
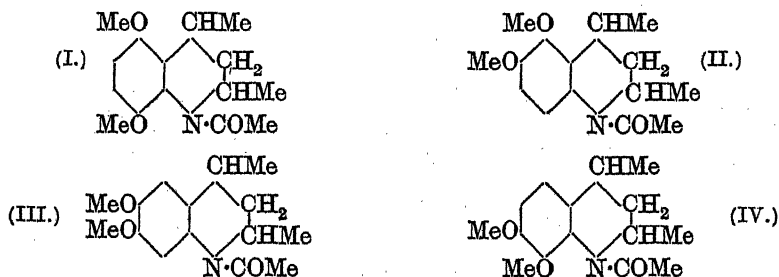
obtained by the following methods. Aminoquinol dimethyl ether condenses with acetylacetone to form an intermediate (V) which is changed by sulphuric acid to 5 : 8-dimethoxy-2 : 4-dimethyl-quinoline (VI).

Similarly, 4-aminoveratrole yields the quinoline (VII) and the *N*-acetyltetrahydro-derivative (III), whilst (VIII) and (IV) are as readily obtained from 3-aminoveratrole. It was more difficult to

obtain a 5 : 6-dimethoxyquinoline derivative not containing a substituent in position 8, but the preparation of the compound (II)

(VII.)

Me

MeO
MeO
Me
N

Me

MeO
MeO
Me
N

(VIII.)
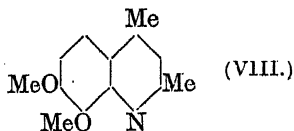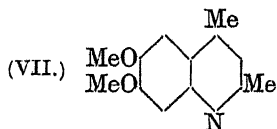
was ultimately achieved by blocking position 8 with a bromine atom which could subsequently be removed by reduction. 5-Bromo-4-aminoveratrole and acetylacetone yield the substituted anilide (IX), which may be dehydrated by careful treatment with concentrated sulphuric acid so as to produce a bromodimethoxydimethyl-quinoline (X). On reduction with sodium and alcohol, a bromine-free dimethoxydimethyltetrahydroquinoline (XI) is obtained. Unfortunately the acetyl derivative (II) could not be crystallised and it may be mentioned that, on account of the stereoisomerism which is due to the existence of the methyl groups in the *cis*- and *trans*-positions in the tetrahydroquinolines, poor yields of homogeneous, crystalline acetyl derivatives were obtained in all cases.

MeO COMe

MeO
CH
CMe
Br NH

(IX.)

MeO Me

MeO
Me
Br N

(X.)

MeO CHMe

MeO
CH₂
CHMe
NH

(XI.)
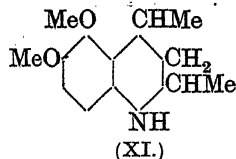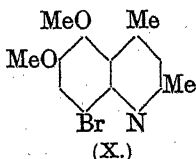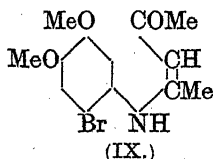
The behaviour of the standards (I, II, III, IV) with nitric acid in acetic acid solution was fortunately such as to permit of definite conclusions concerning the positions of the methoxy-groups in brucine being drawn. The 7 : 8-dimethoxy-derivative (IV) gives no coloration at all, whilst (II) develops a yellow coloration and the same is true of (I), a definite nitro-derivative (XII) being isolated in this case. Brucine cannot, therefore, have the arrangement of methoxyl groups proposed in Part I (Perkin and Robinson, J., 1910, **97**, 305).

(XII.)

MeO CHMe

NO₂
CH₂
CHMe
MeO N·COMe

MeO
MeO
CH₂·CH:CH₂
NH·COMe

(XIII.)
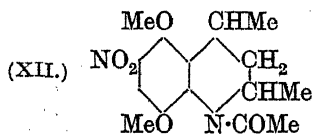
The remaining isomeride, namely, *N*-acetyl-6 : 7-dimethoxy-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (III), exhibits a reaction with nitric acid which is almost identical in colour and tone and persistence on dilution with that characteristic of brucine. We then experimented with similarly constituted amides and found

that this reaction is given by 5-bromo-4-acetylaminoveratrole (Jones and Robinson, J., 1917, **111**, 903), 6-acetylaminohomo-veratrole (Luff, Perkin, and Robinson, J., 1910, **97**, 1131), acetyl-aminosafrole (Foulds and Robinson, J, 1914, **105**, 1963), and 5-acetylamino-4-allylveratrole (XIII). It appears, therefore, that 6-substituted-3 : 4-dialkyloxyacylanilides exhibit the nitric acid reaction of brucine. There is, nevertheless, one important differ-ence, and that is the very much greater delicacy of the reaction in the case of brucine. The orange-red colour is produced with the alkaloid in acetic acid solution with concentrations of nitric acid which leave the synthetical compounds quite unchanged. Great significance undoubtedly attaches to this fact and it is for this reason that we state our conclusions from these experiments in the following propositions.

(1) Brucine contains two methoxyl groups in the ortho-position to each other in a benzene ring, and the quinones from brucine and its derivatives are o-quinones.

(2) If brucine contains a benzene ring bearing only *four sub-stituents*, then these are arranged as shown in the expression XIV.

MeO— / \ —R   MeO / C≡   CH   CH$_2$
MeO— \ / —N=   MeO / \ / R \ N— / CO—   MeO· NO$_2$ C—
                                                    MeO   CO —
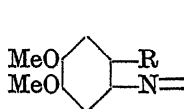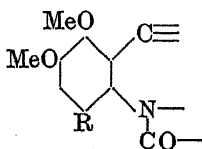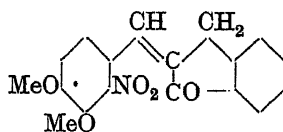
(XIV.)   (XV.)   (XVI.)

(3) In case the benzene ring bears more than four substituents, such arrangements as XV are possible. An alternative statement is that there can be no unsubstituted position in the benzene nucleus para to either of the methoxyl groups. The schemes given by Leuchs and Taube (*Ber.*, 1924, 57, 1092) to represent the possible course of the opening of the benzene ring of cacothelin under the influence of bromine can only with difficulty be recon-ciled with the above conclusions, although the final result can readily be explained. In considering the mechanism of the process the possibility of molecular rearrangement must not be overlooked in the case of a molecule containing so many oxygen and bromine atoms at close quarters. Finally, we were unable to reduce 2'-nitro-3' : 4'-dimethoxy-2-benzylidene-1-hydrindone (XVI) to a quinoline derivative, although the process works well with the related 6-nitro-piperonylidenehydrindone (Armit and Robinson, J., 1922, **121**, 831). This result is clearly due to steric hindrance exerted on the nitro-group, and a quite similar case has been recorded by Rilliet (*Helv. Chim. Acta*, 1922, 5, 547). 6-Nitroveratrylidene-*p*-toluidine

can be readily reduced by aqueous alcoholic sodium sulphide to an amino-derivative, but this was not found possible in the case of the Schiff base derived from 2-nitroveratraldehyde.

EXPERIMENTAL.

β-2 : 5-*Dimethoxyanilinopropenyl Methyl Ketone* (V).—2 : 5-Di-methoxyaniline is best obtained by reduction of nitroquinol dimethyl ether with iron filings and dilute acetic acid at 80—95° in a digester fitted with two propeller blades revolving in opposite directions. Almost 60% is obtained in snow-white crystals by steam distillation, and a further 30% may be recovered from the aqueous distillate by extraction with benzene. A mixture of the base (45 g.) and acetylacetone (32 g.) was gently boiled under reflux for 30 minutes, and the product, washed with water, was collected by ether. The dry residue (58 g.) was a brown oil which gradually crystallised. The compound is readily soluble in most organic solvents, but can be crystallised from ether in colourless, hexagonal plates, m. p. 55° (Found : C, 66·5 ; H, 7·4. $C_{13}H_{17}O_3N$ requires C, 66·4 ; H, 7·3%). The substance is readily hydrolysed by dilute acids, yielding its generators.

5 : 8-*Dimethoxy*-2 : 4-*dimethylquinoline* (VI).—Acetylacetone-2 : 5-dimethoxyanilide (30 g.) was carefully added to concentrated sulphuric acid (180 g.), and the dark greenish-yellow solution was then heated on the steam-bath for 10 minutes and poured into water. On cooling, the sulphate of the quinoline derivative separated in bright yellow needles, and on the addition of sodium hydroxide the *base* itself was obtained as a grey solid (24 g.), which was crystallised from aqueous alcohol and from ethyl acetate (Found : C, 71·8 ; H, 6·8. $C_{13}H_{15}O_2N$ requires C, 71·9 ; H, 7·0%). The base is readily soluble in the simple alcohols, moderately soluble in benzene or chloroform, and but sparingly soluble in ether. It crystallises in slender, colourless needles, m. p. 107°, and is characterised by the intense yellow colour of its salts. The *hydrochloride* is sparingly soluble in cold water and crystallises from acetone in yellow needles, m. p. 235—237° (decomp.). The *picrate*, m. p. 190° with previous darkening, crystallises from alcohol in small, well-defined, yellow prisms.

5 : 8 - *Dimethoxy*-2 : 4 - *dimethyl* - 1 : 2 : 3 : 4 - *tetrahydroquinoline* (Formula corresponding with I).—Sodium (30 g.), cut in small pieces, was added to a boiling solution of 5 : 8-dimethoxy-2 : 4-dimethylquinoline (20 g.) in absolute ethyl alcohol (300 c.c.) under reflux. When all the metal had disappeared, the alcohol was removed by distillation in steam, and the brown oil which separated was collected and dried in ether and distilled under diminished

pressure, 17 g. of a colourless, viscous oil, b. p. 170—172°/10 mm., being obtained (Found : C, 70·3; H, 8·7. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7%). This strong base is volatile in steam to some extent and is odourless. A solution of its hydrochloride gives no colour with ferric chloride in the cold, but, on warming, a permanganate colour develops and this fades to reddish-brown. It gives a dark blood-red coloration with concentrated nitric acid or with dilute nitric acid and a trace of sodium nitrite.

The N-*acetyl* derivative (I) was prepared by acetylating the base with twice its weight of acetic anhydride for 2 hours in the cold and then for 15 minutes on the steam-bath. The excess of reagent was decomposed by dilute hydrochloric acid, and the oil washed with water and dried; after 3 days, the material had largely solidified. The substance crystallised from benzene–ligroin in small, colourless, rhombic plates, m. p. 85—86° (Found : C, 68·2; H, 8·1. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). The yield was less than 60% and the mother-liquors contained an uncrystallisable oil. This derivative is readily soluble in most organic solvents. It dissolves in sulphuric acid to a yellowish-green solution which changes to green and then to brown; on heating, the colour changes are through brown to reddish-violet, red, and orange.

6 - *Nitro* - 1 - *acetyl* - 5 : 8 - *dimethoxy* - 2 : 4 - *dimethyl* - 1 : 2 : 3 : 4 - *tetrahydroquinoline* (XII).—1-Acetyl-5 : ⁗8-dimethoxy-2 : 4-dimethyltetrahydroquinoline (2 g.) was dissolved in acetic acid (15 c.c.), and nitric acid (4 c.c.; d 1·42) gradually introduced. After an hour the mixture was added to water, and the yellow solid was washed and dried (2 g.) (Found : C, 58·3; H, 6·8. $C_{15}H_{20}O_5N_2$ requires C, 58·4; H, 6·5%). The substance is readily soluble in most organic solvents and crystallises in stellar aggregates of long, flat, needles, m. p. 127°, from a mixture of ethyl acetate and ligroin. The yellow solution in sulphuric acid remains unchanged on the addition of a trace of potassium dichromate and this indicates that the *p*-position to the quinoline nitrogen is occupied.

6.-*Acetylamino* - 1 - *acetyl* - 5 : 8 - *dimethoxy* - 2 : 4 - *dimethyl* - 1 : 2 : 3 : 4 - *tetrahydroquinoline.*—Nitro - 1 - acetyldimethoxydimethyltetrahydroquinoline (1 g.) was gradually introduced into a well-stirred mixture of acetic acid (0·2 c.c.), iron filings (10 g.), and water (25 c.c.) at 80—90°, and the agitation continued for an hour. Alternatively, reduction may be effected with boiling aqueous sodium sulphide. In either case, a brown basic oil could be isolated, but could not be induced to crystallise. It reacted vigorously with acetic anhydride, a white, crystalline powder separating at once. This derivative crystallises from ethyl acetate–light petroleum in small,

colourless prisms, m. p. 171° (Found : C, 63·7 ; H, 7·4. $C_{17}H_{24}O_4N_2$
requires C, 63·7 ; H, 7·6%).

β-6-*Bromo*-3 : 4-*dimethoxyanilinopropenyl Methyl Ketone* (IX).—
In the preparation of 5-bromo-4-aminoveratrole by the hydrolysis
of its acetyl derivative with methyl-alcoholic potassium hydroxide
(Jones and Robinson, J., 1917, **111**, 913 ; Simonsen and Rau,
J., 1918, **113**, 787) we have found a modification of the isolation
process serviceable. After the hydrolysis the excess of alkali is
neutralised with carbon dioxide, and the filtered solution, cooled
in ice, is treated with a slight excess of hydrochloric acid. The
hydrochloride of the base which separates is washed with alcohol
until colourless and dried, the yield being satisfactory. This salt
crystallises from methyl alcohol in lustrous prisms, m. p. 216—218°
(decomp.). It is sparingly soluble in cold water, but if the solution
be heated, decomposition occurs and a deep purple coloration is
soon produced. This is, of course, traceable to the presence of a
positive bromine atom, the activation of which is due to the amino-
group in the *o*-position. A striking confirmation of this view is
to be found in the fact that a solution of the salt in moderately
concentrated hydrochloric acid can be boiled without decomposition.
In view of this curious decomposition,* the base was set free from
a *cold* dilute solution of the hydrochloride by means of sodium
hydroxide. This instability of the bromoaminoveratrole necessi-
tates the observance of precautions against overheating in the
course of its condensation with acetylacetone, failing which, rapid
and complete decomposition ensues. A mixture of the base (23 g.)
and acetylacetone (15 g.) was gently boiled for 10 minutes, and
the dark, purplish-red product washed with water, dried, and the
solvent removed, leaving an oily residue which slowly crystallised.
The substance is readily soluble in the common organic solvents
with the exception of light petroleum and crystallises from aqueous
alcohol in nearly colourless needles, m. p. 78—79° (Found : C,
50·4 ; H, 5·4. $C_{13}H_{16}O_3NBr$ requires C, 49·7 ; H, 5·1%).

8-*Bromo*-5 : 6-*dimethoxy*-2 : 4-*dimethylquinoline* (X).—This sub-
stance is conveniently obtained under the following conditions,
which are the result of numerous trials and cannot be usefully
varied so far as our experience goes. The acetylacetonebromo-
dimethoxyanilide (10 g.) was gradually added to well-cooled and
stirred concentrated sulphuric acid (80 g.) and the mixture was finally
heated at 60° for a few minutes and then allowed to remain for ½

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* One of the products of the reaction is a neutral substance containing
bromine and separating from ethyl acetate as a dark brown, crystalline
powder, m. p. 160—161°. This compound dissolves in sulphuric acid to a
pure blue solution.

hour. The product was added to ice and water, the cold, dark yellow solution basified with sodium hydroxide, and the solid collected. The solution of the base in hot dilute hydrochloric acid was treated with animal charcoal and the base, again isolated from the lemon-yellow solution, could be crystallised from aqueous methyl alcohol in faintly yellow, slender needles, m. p. 74—75° (yield 70%) (Found : C, 52·2 ; H, 4·6. $C_{13}H_{14}O_2NBr$ requires C, 52·7 ; H, 4·7%). The salts of the base are all yellow and the *hydrochloride* crystallises from acetone in small, elongated prisms, m. p. 136—138°.

5 : 6-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XI)..—Sodium (10 g.) was gradually added to a boiling solution of 8-bromo-5 : 6-dimethoxy-2 : 4-dimethylquinoline (7 g.) in absolute alcohol (100 c.c.), and when all the metal had disappeared the alcohol was distilled in steam and the base collected by ether. A pale yellow oil (4 g.), b. p. 166—167°/10 mm., was isolated by fractionation (Found : C, 70·5 ; H, 8·9. $C_{13}H_{19}O_2N$ requires C, 70·6 ; H, 8·7%). A dilute solution of the hydrochloride of this base gave a beautiful pink coloration changing to wine-red on the addition of ferric chloride. An oily orange-yellow nitrosoamine was precipitated by the addition of sodium nitrite to the very pale yellow solution in dilute nitric acid. The *acetyl* derivative (II) was obtained by a gentle process of acetylation with acetic anhydride, but could not be induced to crystallise. Its solution in sulphuric acid became intense-reddish-brown on the addition of a drop of nitric acid, and when the solution in glacial acetic acid was treated with nitric acid a yellow coloration resulted.

β-3 : 4-*Dimethoxyanilinopropenyl Methyl Ketone*.—A mixture of 4-aminoveratrole (45 g.) (compare Fargher, J., 1920, 117, 865) and acetylacetone (32 g.) was gently boiled for 30 minutes, and the product isolated as in the case of the 5 : 8-isomeride. The substance is readily soluble in most organic solvents except ether and ligroin and may be crystallised from ethyl acetate–ligroin and from ligroin in minute prisms, m. p. 79° (Found : C, 66·2 ; H, 7·4. $C_{13}H_{17}O_3N$ requires C, 66·4 ; H, 7·3%).

6 : 7-*Dimethoxy*-2 : 4-*dimethylquinoline* (VII).—Acetylacetone-3 : 4-dimethoxyanilide (40 g.) was gradually added to cold sulphuric acid (240 g.), and the solution heated for 10 minutes on the steam-bath. The oil, which was obtained from the diluted liquid on basification, crystallised and was collected, washed, and dried (29 g.). The substance is sparingly soluble in ether and ligroin, otherwise readily soluble in organic solvents, and may be conveniently crystallised from dry acetone, separating in small, colourless, rhombic prisms, m. p. 81·5—82° (Found : C, 71·7 ; H, 7·0. $C_{13}H_{15}O_2N$ requires C, 71·9 ; H, 7·0%). In contradistinction to

some of the isomeric quinoline derivatives the salts of this sub-
stance are colourless. The *hydrochloride* separates from acetone as
a white powder, m. p. 286° (decomp.), and the *picrate* crystallises
from the same solvent in slender, yellow needles, m. p. 239°, and is
very sparingly soluble. Ferric chloride added to acid solutions of
the base produces no distinctive reaction.

6 : 7-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (For-
mula corresponding with III).—6 : 7-Dimethoxydimethylquinoline
(20 g.) in boiling absolute alcohol (300 c.c.) was reduced by
the gradual addition of sodium (30 g.). When complete solution
occurred, the alcohol was removed by distillation in steam, and
the pale brown oil collected by ether and distilled under diminished
pressure. There resulted 16·5 g. of a viscous, light yellow oil,
b. p. 186—189°/12 mm., which on standing crystallised. The
substance crystallised from ligroin in colourless, feathery needles,
m. p. 73—74° (Found : C, 70·4; H, 8·8. $C_{13}H_{19}O_2N$ requires C,
70·6; H, 8·7%). The golden-yellow *picrate* has m. p. 145°
(decomp.). A solution of the base in dilute hydrochloric acid
gradually acquires a pure olive-green colour after the addition of
ferric chloride. On heating, the colour appears more rapidly and
suddenly fades to a pale lemon-yellow. The formation of a yellow
nitrosoamine was observed.

1-*Acetyl*-6 : 7-*dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinol-
ine* (III).—A solution of the 6 : 7-dimethoxydimethyltetrahydro-
quinoline (10 g.) in acetic anhydride (20 g.) was kept for 2
hours and then heated on the steam-bath for 15 minutes. After
the product, decomposed by water, had been washed with dilute
hydrochloric acid, partial crystallisation occurred and about 5 g.
of solid could be collected. The substance crystallised from ligroin
(b. p. 70—80°) in colourless, well-formed, rhombic prisms, m. p.
118°, readily soluble in most organic solvents (Found : C, 68·5;
H, 8·2. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). The pale yellow
solution in sulphuric acid becomes bright orange-red on the addition
of a trace of nitric acid, and the reaction is identical with that
exhibited by brucine in similar circumstances. The colour fades,
however, a little more rapidly than that produced by brucine. If
a few drops of nitric acid are added to a solution in acetic acid,
the yellow coloration at first obtained rapidly deepens to orange-red
and the colour is identical with that produced by brucine when
treated in the same way. On dilution, the appearance of the
liquid is identical in the two cases. Nevertheless, the brucine
reaction is exhibited at much the lower concentration of nitric
acid.

β-2 : 3-*Dimethoxyanilinopropenyl Methyl Ketone.*—A mixture of

3-aminoveratrole * (25 g.) and acetylacetone (17 g.) was boiled for a few minutes, and the resulting oil was well washed with water and dried (36 g.) (Found : C, 66·1; H, 7·3. $C_{13}H_{17}O_3N$ requires C, 66·4; H, 7·3%). This substance could not be crystallised and on exposure to air the pale yellow oil darkened to orange-red.

7 : 8 - *Dimethoxy* - 2 : 4 - *dimethylquinoline* (VIII).—Acetylacetone-2 : 3-dimethoxyanilide (32 g.) was carefully added to cooled and stirred sulphuric acid (160 g.), and the dark brown mixture heated for 10 minutes on the steam-bath. The base was isolated in the usual manner and 25 g. of a pale yellow, viscous oil, b. p. 189—191°/10 mm., were collected (Found : C, 71·6; H, 7·1. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 7·0%). The *hydrochloride* crystallises from acetone in pale yellow prisms, m. p. 145°.

7 : 8-*Dimethoxy*-2 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (Formula corresponding with (IV).—The quinoline derivative (20 g.) just described was reduced by sodium (30 g.) in boiling ethyl-alcoholic solution (300 c.c.), and the tetrahydro-derivative isolated in the usual manner. A colourless oil (18 g.), b. p. 168—170°/12 mm., was obtained (Found : C, 70·3; H, 8·5. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·7%).

The reactions of the substance resemble those of the 6 : 7-isomeride. Its N-*acetyl* derivative (IV) was obtained exactly as in other cases, and 10 g. of the base yielded only 5 g. of the solid substance. The latter was several times crystallised from light petroleum and then from aqueous methyl alcohol, separating in colourless needles, m. p. 98—99° (Found : C, 68·3; H, 8·1. $C_{15}H_{21}O_3N$ requires C, 68·4; H, 8·0%). An alcoholic solution was diluted with water and at first clouded, but on further dilution became clear, and on long standing deposited well-shaped, rhombic plates. The solution in acetic acid gives no coloration on the addition of a little nitric acid and only a pale yellow when a considerable volume of the reagent is introduced.

5-*Nitro*-4-*allylveratrole* (compare formula XIII).—Nitric acid (65 g.; d 1·42) was added drop by drop during 30 minutes to a vigorously stirred solution of eugenol methyl ether (80 g.) in acetic acid (320 c.c.), cooled in a mixture of ice and salt. After further stirring and cooling for 3 hours, the mixture was added to 3 litres of water, and the precipitated nitro-derivative washed and dried (80 g.). The substance is readily soluble in most organic solvents, but crystallises from light petroleum in slender, lemon needles, m. p. 44° (Found : C, 59·4; H, 5·6. $C_{11}H_{13}O_4N$ requires C, 59·2;

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* In the preparation of this base (Gibson, Simonsen, and Rau, J., 1917, **111**, 79) by heating 2-amino-3 : 4-dimethoxybenzoic acid with glycerol, mechanical stirring was found to be a considerable advantage.

H, 5·8%).* The solution in concentrated sulphuric acid is bright red.

5-*Acetylamino*-4-*allylveratrole* (XIII).—Granulated tin (20 g.) and concentrated hydrochloric acid (30 c.c.) were gradually added to a cooled and agitated mixture of 5-nitro-4-allylveratrole (10 g.), stannous chloride (10 g.), hydrochloric acid (10 c.c.), and acetic acid (35 c.c.), and the stirring was continued until reduction was completed. Zinc was added to eliminate tin, the diluted, filtered solution rendered strongly alkaline with sodium hydroxide, and the oily base (6 g.) collected by ether. When added to twice its weight of acetic anhydride, heat was evolved and the mixture rapidly set to a crystalline mass. The substance was washed, isolated, and crystallised from aqueous methyl alcohol and from ethyl acetate–ligroin, separating in micaceous, colourless needles, m. p. 126—127° (Found : C, 66·0; H, 7·2. $C_{13}H_{17}O_3N$ requires C, 66·3; H, 7·3%). The substance is readily soluble in most organic solvents. A solution of the derivative in sulphuric acid or in acetic acid gives the characteristic brucine orange-red reaction on the addition of nitric acid.

2'-*Nitro*-3' : 4'-*dimethoxy*-2-*benzylidene*-1-*hydrindone* (XVI).—A stream of hydrogen chloride was passed through a solution of 2-nitroveratraldehyde (21·1 g.) and α-hydrindone (13·2 g.) in acetic acid (250 c.c.) during 1·5 hours. After several hours, the yellow crystals which had separated were collected and the filtrate was again saturated with hydrogen chloride. This caused a further crystallisation and by repetition of the process 17·8 g. of solid were collected. The substance was several times crystallised from alcohol, in which it was very sparingly soluble, and obtained in yellow prisms, m. p. 156—176° (Found: C, 66·3; H, 4·7. $C_{18}H_{15}O_5N$ requires C, 66·4; H, 4·7%). This material is probably a mixture of stereoisomerides, but it was not found possible to separate these by crystallisation. The solution in sulphuric acid is orange-red. All attempts to obtain a quinoline derivative by reduction were fruitless.

6'-*Nitro*-3' : 4'-*dimethoxy*-2-*benzylidene*-1-*hydrindone*,
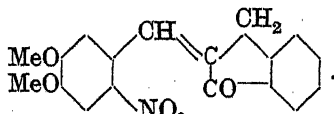
—This substance was obtained from 6-nitroveratraldehyde in 50% yield by a process exactly similar to that just described in the case of an isomeride. The compound is very sparingly soluble in most

* This substance was first prepared and analysed by Miss E. E. P. Hamilton at the University of Sydney.

organic solvents and is most conveniently crystallised by the addition of alcohol to its solution in hot pyridine, when brownish-yellow needles, m. p. 211°, separate (Found: C, 66·3; H, 4·9. $C_{18}H_{15}O_{5}N$ requires C, 66·4; H, 4·7%). The solution in sulphuric acid is bright red. By reduction in hot acetic acid solution *dimethoxy-indenoquinoline* is produced, the *hydrochloride* of which crystallises from dilute hydrochloric acid in minute prisms, m. p. 251—252° with previous softening, and gives an intensely bluish-purple, fluorescent solution in alcohol. The free base, m. p. 188—190°, crystallises from benzene–ligroin.

CLXII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXVI. Four Alcohols containing the Vinyl Group and some Esters derived therefrom.*

By JOSEPH KENYON and DOUGLAS ROSEBERY SNELLGROVE.

A LARGE proportion of the work which has hitherto been carried out on the relationship between unsaturation and optical activity suffers from several serious drawbacks which may be classified roughly under three heads :—

1. The compounds examined have frequently been of complicated chemical constitution and have, in addition, possessed one or more of the following disturbing features—

(*a*) have contained more than one asymmetric centre within the molecule,

(*b*) have contained one or more cyclic systems within the molecule,

(*c*) have contained in addition to the ethylenic (or acetylenic) linking other centres of unsaturation such as a phenyl group or a ketonic group.

2. The centre of unsaturation has been remote from the asymmetric carbon atom.

3. The compounds have been solids and their rotatory powers

have necessarily been determined in solution or at high temperatures.

It was therefore considered desirable to prepare optically active compounds each of which should (a) be of simple chemical constitution, (b) contain only one asymmetric carbon atom, (c) contain only one centre of unsaturation, (d) have the centre of unsaturation as near as possible to the asymmetric atom, (e) be liquid at the ordinary temperature.

With this object in view, the first four members of the homologous series of alcohols of the general formula $CH_2:CH\cdot CH(OH)\cdot R$ have been prepared in their optically active modifications. The choice of these alcohols was due, in part, to the fact that the corresponding saturated alcohols, $CH_3\cdot CH_2\cdot CH(OH)\cdot R$, have already been obtained in their optically active forms (Part IV, J., 1913, **103**, 1923), thus allowing of direct comparisons being made of the effect on rotatory power of an ethylenic linking in each of the four pairs of compounds. The results, which are tabulated below, show that the presence of such linking exalts the rotatory power to a very considerable extent.

Specific Rotatory Powers of the Compounds in the Homogeneous Condition.

Saturated compound.	$[a]_D^{20°}$.		Unsaturated compound.
l-Methylethylcarbinol	−13·9°	−33·7°	*l*-Methylvinylcarbinol
Diethylcarbinol	± 0	−35·2	*l*-Ethylvinylcarbinol
l-n-Propylethylcarbinol	− 1·97	−28·2	*l-n*-Propylvinylcarbinol
l-n-Butylethylcarbinol	− 8·13	−25·0	*l-n*-Butylvinylcarbinol *

* Delaby (*Bull. Soc. chim.*, 1923, **33**, 602), by employing the method of resolution used by Pickard and Kenyon, has prepared *l-n*-butylvinylcarbinol of $[a]_D^{20°}$ −23·3°. Both *d*- and *l*-forms of this alcohol are described in the present communication with $[a]_D$ ±25·0°. Delaby's paper, which appeared during the course of this work, gives no experimental details of the resolution.

On the other hand, when comparisons are made of the specific rotatory powers of the hydrogen phthalates of these alcohols, the exalting effect of unsaturation on rotatory power becomes much less pronounced, and is in one case entirely suppressed, as is shown by the following results :—

Specific Rotatory Powers of the Hydrogen Phthalates (c = 5 *in Ethyl Alcohol*).

Saturated compound of	$[a]_D$.		Unsaturated compound of
l-Methylethylcarbinol	−38·4°	−40·5°	*l*-Methylvinylcarbinol
Diethylcarbinol	± 0	−26·5	*l*-Ethylvinylcarbinol
l-n-Propylethylcarbinol	− 7·26 †	−16·0	*l-n*-Propylvinylcarbinol
l-n-Butylethylcarbinol	−19·82	−12·6	*l-n*-Butylvinylcarbinol

† Compare Part VII, J., 1914, **105**, 2236.

The above table illustrates the need for simplicity of chemical structure in compounds employed in attacking optical problems.

The specific and molecular rotatory powers of ethylvinylcarbinol, which are the highest of the series, are in agreement with the prediction of Frankland (J., 1899, **75**, 868) that some irregularity (maximum or minimum) in rotatory power might be manifested by that member of a homologous series of compounds which contains five carbon atoms. This result is. analogous to that shown by d-methyl-n-propylcarbinol in ethyl-alcoholic solution (Part IV, J., 1913, **103**, 1929); the molecule of each of these alcohols consists essentially of a chain of five carbon atoms.

In order to elucidate the configurational relation between a lævorotatory unsaturated alcohol and the corresponding saturated alcohol of the same sign of rotation, l-n-butylvinylcarbinol in acetic acid solution was reduced with hydrogen and colloidal platinum. The l-n-butylethylcarbinol produced was lævorotatory, thus showing that the sign of rotation had not been affected; moreover, the carbinol possessed the same magnitude of rotatory power as the l-n-butylethylcarbinol prepared by the direct resolution of the dl-alcohol.

Some physical properties of the two specimens of this alcohol are compared below :—

	l-Butylethylcarbinol obtained	
	(a) by reduction of l-butylvinylcarbinol.	(b) by direct resolution of dl-butylethylcarbinol.
$[\alpha]_D^{20°}$	$-8\cdot11°$	$-8\cdot13°$
$d_4^{20°}$	$0\cdot8225$	$0\cdot8227$
$n_D^{25°}$	$1\cdot4205$	$1\cdot4204$
M. p. of hydrogen phthalate	47—$48°$	47—$48°$
$[\alpha]_D^{alc.}$ „ „ „	$-19\cdot84°$	$-19\cdot82°$

Moreover, the acetate of l-n-butylvinylcarbinol was reduced by the same method; the results are shown by the diagram

l-n-butylvinylcarbinol $\xrightarrow{\text{reduction}}$ l-n-butylethylcarbinol
$[\alpha]_D^{20°} - 25\cdot0°$ $[\alpha]_D^{20°} - 8\cdot11°$

l-n-butylvinylcarbinyl acetate
$[\alpha]_D^{20°} + 4\cdot36°$
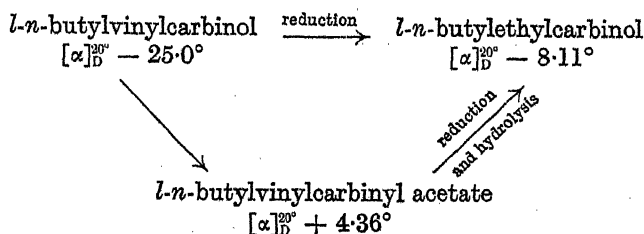
In addition to establishing the identity of the reduced alcohol, these data furnish very strong support for the view that optical purity has been reached in the resolution of the alcohols belonging to both these homologous series : the probability that (incomplete)

resolution would take place to exactly the same extent in the cases of *l*-butylvinylcarbinol and *l*-butylethylcarbinol must bo exceedingly small.

The rotatory powers of unsaturated compounds hitherto have been determined almost entirely with light of one wave-length—the D line, so that the optical rotatory dispersion of unsaturated compounds of simple chemical constitution is a subject about which little is known. It became, therefore, of particular interest to measure the optical rotatory dispersion of these four unsaturated alcohols. In each case there was sufficient alcohol to fill a 2-dcm. tube, and the rotatory powers were measured for light of wavelengths ranging from $\lambda = 6708$ to $\lambda = 3780$ Å.U. The rotatory powers were measured also of the alcohols in the homogeneous state at temperatures between 20° and the boiling points.

By applying to the observed rotatory powers the method of calculation used by Lowry in the case of *sec.*-octyl alcohol (J., 1924, **125**, 1596) dispersion equations have been obtained and also values for the constants k_0 and λ_0, for the four alcohols. A one-term dispersion equation containing the calculated values for the " constants " gives rotatory powers in agreement with the experimental data in each case, thus showing that the alcohols possess simple rotatory dispersion within the experimental range.

The equations are :—

Å. U.

d-Methylvinylcarbinol :	$[\alpha]_\lambda^{18°} = 9\cdot920/(\lambda^2-0\cdot0528)$	$\lambda_0 = 2300$
d-Ethylvinylcarbinol :	$= 10\cdot27/(\lambda^2-0\cdot0554)$	$= 2380$
l-n-Propylvinylcarbinol :	$= 8\cdot331/(\lambda^2-0\cdot0574)$	$= 2400$
d-n-Butylvinylcarbinol :	$= 7\cdot533/(\lambda^2-0\cdot0582)$	$= 2410$
d-n-Butylvinylcarbinol in *cyclo*hexane solution :	$= 7\cdot787/(\lambda^2-0\cdot0573)$	$= 2400$

On comparing the values of λ_0 for these alcohols with corresponding values for the saturated alcohols, two points are brought out : (*a*) unsaturation increases λ_0, bringing it nearer the visible region, as would be expected, and (*b*) with increasing molecular weight, λ_0 increases in the " vinyl " series and diminishes in the " ethyl " series.

R.	" Ethyl series." *	" Vinyl series."
Methyl	1610	2300
Ethyl	—	2380
n-Propyl	[1200] †	2400
n-Butyl	1530	2410
n-Amyl	1430	—

* Lowry, Pickard, and Kenyon, J., 1914, **105**, 94.
† Rotation too small to give trustworthy values.

The refractive indices of these four alcohols have been determined and a comparison of these with the values for the corresponding saturated alcohols shows clearly the exalting influence of

the double bond. A comparison of the densities shows that in each case the unsaturated alcohol has the greater density :—

	$D_{4°}^{20°}.$	$n_D^{20°}.$		$D_{4°}^{20°}.$	
Methylvinylcarbinol	0·8320	1·4120	1·3954	0·8080	Methylethylcarbinol
Ethylvinylcarbinol	0·8406	1·4218	1·4094	0·8198	Ethylethylcarbinol
n-Propylvinylcarbinol	0·8370	1·4268	1·4141	0·8213	n-Propylethylcarbinol
n-Butylvinylcarbinol	0·8360	1·4337	1·4206	0·8227	n-Butylethylcarbinol

Several esters derived from two of these unsaturated alcohols and the n-fatty acids and benzoic acid have been prepared : their rotatory powers and other physical properties are given in the experimental part. As is the case with the aliphatic esters derived from the ethylalkylcarbinols, they have rotatory powers of opposite sign to that of the alcohol from which they are derived.

Specific Rotatory Powers in the Homogeneous State at 20°.

	$[\alpha]_D^{20°}.$	
	Alcohol.	Acetate.
l-n-Butylvinylcarbinol	—25·0°	+ 4·36°
l-n-Butylethylcarbinol	— 8·13	+16·5

These data furnish additional support for the view expressed above—that in attempting to unravel the difficult problem of the relation between unsaturation and optical activity the compounds examined should be of the simplest possible chemical constitution.

All these esters exhibit complex rotatory dispersion; and so also do the esters derived from n-fatty acids and a large number of saturated aliphatic alcohols which have been described in previous parts of this series of communications. In order to explain why complex rotatory dispersion is exhibited by esters derived from alcohols which themselves show simple rotatory dispersion, advantage has been taken (J., 1914, **105**, 830) of the view put forward by Smedley (J., 1909, **95**, 931) that the carboxyl group can be represented by the two formulæ $-C{<}_{OH}^{O}$ and $-C{<}_{OH}^{O}$; the esters can thus be assumed to consist of equilibrium mixtures derived from the two forms of the carboxylic acid.

Recently Scheibler and Voss (*Ber.*, 1920, **53**, 388) have prepared potassio-derivatives of esters and they suggest the formulation of esters in such a manner that the presence of a mobile hydrogen atom is indicated; thus, for ethyl acetate

$$CH_3 \cdot C{<}_{OEt}^{O} \quad \rightleftharpoons \quad CH_2 : C{<}_{OEt}^{OH}.$$
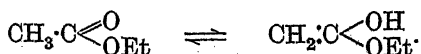
An alternative formulation of the isodynamic forms of these esters therefore appears available. This, however, is not the case, since

the formates derived from two of the above alcohols, as well as formates derived from methylethylcarbinol, methyl-*n*-hexylcarbinol and ethyl-*n*-hexylcarbinol (Part XIII, J., 1923, **123**, 1), exhibit complex rotatory dispersion. The formula of a formic ester does not permit the mobility of the hydrogen atom attached to the carbonyl group, unless the presence of bivalent carbon in the molecule is assumed; the suggestion of Scheibler and Voss cannot be considered in this connexion. A further proof of its inapplicability is to be found in the case of benzylmethylcarbinyl trimethylacetate,* which exhibits complex rotatory dispersion and yet does not possess a mobile hydrogen atom attached to the carbon atom immediately adjacent to the ester group.

Experimental.

Preparation of the Inactive Alcohols.—These alcohols, which have been very briefly described by Delaby (*loc. cit.*), were prepared by the interaction of acraldehyde † and the appropriate Grignard reagent, and were obtained in yields of 35—48%. The boiling points at the ordinary pressure were : Methylvinylcarbinol (after standing for several days over freshly ignited barium oxide), 96—98°; ethylvinylcarbinol, 113—114·5°; *n*-propylvinylcarbinol, 133—135°; *n*-butylvinylcarbinol, 153—155°.

The purity of each of the alcohols was determined by titration with a standard solution of bromine.

The hydrogen phthalic esters of the inactive alcohols were prepared by heating the alcohol with phthalic anhydride (in 10% excess) at 100° for 10 hours, and their purity was checked by titration with standard sodium hydroxide solution. Their properties are as follows :—

Melting Points.

	dl-.	*d*-.	*l*-.
Methylvinylcarbinyl hydrogen phthalate	+5°	52—53°	52—53°
Ethylvinylcarbinyl hydrogen phthalate	oil	oil	oil
n-Propylvinylcarbinyl hydrogen phthalate ...	‡62—63°	—	58—60°
n-Butylvinylcarbinyl hydrogen phthalate ...	56—57	50—52°	50—52

‡ Too soluble in all solvents for satisfactory crystallisation. The other solid esters were crystallised (generally in the form of prismatic needles) from ligroin.

Resolution of Methylvinylcarbinol.—Brucine (870 g.) was added to a warm solution of the hydrogen phthalate (400 g.) in

* Unpublished experiment.

† The acraldehyde was prepared by the excellent method of Moureu (*Ann. Chim.*, 1921, **15**, 158) and obtained in yields of about 65%. The product which distilled at 53·5—54·5° was stabilised by the addition of 0·5% of its weight of quinol.

acetone (2 litres), and the mixture heated until all the brucine had dissolved; the solution was then concentrated to half its bulk. The *brucine* salt, which separated on cooling in leaflets (m. p. 120—122°), was recrystallised seventeen times from acetone, when optical purity was reached. By the systematic working up of the mother-liquors, a further quantity of pure brucine salt was obtained, bringing the total to 140 g. The hydrogen phthalate obtained from this brucine salt crystallised from light petroleum in long, prismatic needles, m. p. 52—53°, $[\alpha]_D + 40·5°$ ($c = 5$ in ethyl alcohol).

The partly active ($[\alpha]_D - 18°$) hydrogen phthalate obtained from the more soluble fractions of the brucine salt was combined with strychnine, morphine, quinine, cinchonine, cinchonidine, and quinidine, but none of these salts was obtained in the solid condition. The following procedure, however, gave the pure *l*-hydrogen phthalate. A sample of the ester ($[\alpha]_D - 18°$) was dissolved in warm ligroin with the addition of a few drops of ether; after a few days, a mixture of oil and crystalline material separated. The crystals had $[\alpha]_D - 30·0°$ (in ethyl alcohol), and the oil $[\alpha]_D - 9°$ (in ethyl alcohol). After eight crystallisations from ligroin, the crystalline hydrogen phthalate reached constancy of melting point (52—53°) and of rotatory power ($[\alpha]_D - 40·6°$ in ethyl alcohol). Both values are in excellent agreement with those of the corresponding *d*-isomeride.

Resolution of Ethylvinylcarbinol.—A solution of the hydrogen phthalic ester of ethylvinylcarbinol (457 g.) and finely-powdered strychnine (655 g.) in excess of absolute ethyl alcohol was concentrated until it was slightly syrupy, cooled, and kept over-night. The crystalline strychnine salt obtained (880 g. of m. p. 159—160°), after twelve recrystallisations, was optically pure. By systematic working up of the various filtrates, a total yield of 260 g. of optically pure strychnine salt was obtained: the hydrogen phthalate derived from the various crops had $[\alpha]_D + 26·2°$ ($c = 5$ in ethyl alcohol). An attempt was made to resolve the hydrogen phthalate by crystallisation of the brucine salt from acetone, but although resolution did occur, it ceased when the specific rotatory power of the hydrogen phthalic ester derived from the least soluble crops of the brucine salt (m. p. 134—135°) reached $[\alpha]_D + 15·5°$ ($c = 5$ in ethyl alcohol). All efforts to increase this value were fruitless, but it was subsequently found that a sample of hydrogen phthalate having $[\alpha]_D + 22·0°$, when converted into brucine salt and crystallised from acetone until constancy of rotatory power was reached, had its rotatory power increased to $[\alpha]_D + 26·3°$—a value almost identical with that exhibited by the ester obtained from the optically pure

strychnine salt. The hydrogen phthalate was obtained as a pale yellow, viscous oil which did not solidify on long standing.

Numerous unsuccessful attempts were made to obtain the optically pure *l*-hydrogen phthalate by fractional crystallisation of salts derived from other alkaloids; the salts were either not crystalline or too soluble for recrystallisation. Partially. active hydrogen phthalate ($[\alpha]_D^{hlc.} - 6\cdot4°$) was combined with benzidine (1 mol.), and the crystalline salt recrystallised several times from benzene. The least soluble fraction was the salt of the *dl*-ester, a microcrystalline powder, m. p. 96—98°.

The hydrogen succinate of ethylvinylcarbinol was therefore prepared (by heating the alcohol with succinic anhydride at 100° for 10 hours), and obtained as a viscous oil showing no tendency to crystallise. The salts of this ester with all the commoner alkaloids were obtained as very soluble gums. On heating the alcohol with diphenic anhydride, the hydrogen diphenate was obtained in crystalline needles, m. p. 55°. The alkaloidal salts of this ester also proved to be unsuitable for crystallisation.

Resolution of n-*Propylvinylcarbinol.*—Strychnine (448 g.) was dissolved in a hot solution of the hydrogen phthalate (325 g.) in absolute ethyl alcohol (1500 c.c.), and the whole concentrated to somewhat less than half its bulk. The *strychnine* salt separated in hard prisms, m. p. 164—166°, and sixteen recrystallisations were necessary before optical purity was reached. After a somewhat laborious working up of the mother-liquors, a total amount of 65 g. of pure strychnine salt, m. p. 170—172°, was obtained. The hydrogen phthalate obtained by the decomposition of this salt was a crystalline mass, m. p. 58—60°, which had $[\alpha]_D - 16\cdot05°$ ($c = 5$ in ethyl alcohol).

The partly dextrorotatory hydrogen phthalate obtained from the more soluble fractions of the strychnine salt was converted into salts with numerous alkaloids, but, except in the case of brucine (see below), these were gums.

Crystallisation from light petroleum of the partly active hydrogen phthalic ester effected little or no separation. Although the hydrogen phthalate of the partly active alcohol is an oil, whilst that of the *dl*-alcohol is a solid of m. p. 62—63°, yet the latter is so excessively soluble in all solvents tried that it crystallises with extreme difficulty. In a similar manner, although the *p*-nitrobenzoate of the partially active alcohol is an oil whilst that of the *dl*-alcohol is a solid (leaflets, m. p. 60—62°), attempts to increase the rotatory power of the partially active ester by crystallisation were unsuccessful. In view of the failure to obtain the pure *d*-hydrogen phthalate, an attempt was made to prepare the

l-hydrogen phthalate by the use of another alkaloid as follows. Hydrogen phthalic ester having $[\alpha]_D$ — 12° was dissolved in acetone and mixed with a molecular quantity of brucine. The *brucine* salt separated in prismatic needles (m. p. 118—120°) which, after five recrystallisations from acetone, reached constancy of rotation. The hydrogen phthalate obtained from this salt had exactly the same rotatory power as that obtained from the strychnine salt.

Resolution of n-*Butylvinylcarbinol.*—A solution of strychnine (645 g.) and hydrogen phthalate (490 g.) in absolute ethyl alcohol (4,000 c.c.), on standing, deposited a crystalline crop of the *strychnine* salt. This resolution proceeded very smoothly and after eight recrystallisations constancy of rotatory power was reached. Altogether 250 g. of pure strychnine salt were obtained, in quadratic plates, m. p. 174—176°; these yielded a hydrogen phthalate, m. p. 50—52°, having $[\alpha]_D$ — 12·6° ($c = 5$ in ethyl alcohol). A sample of hydrogen phthalate (180 g.), having $[\alpha]_D$ — 9°, obtained from the more soluble fractions of the strychnine salt was combined with morphine (224 g.) in ethyl alcohol (500 c.c.). After cooling, the *morphine* salt separated (m. p. 112—114°) and after four recrystallisations was obtained with constancy of rotatory power. Altogether 120 g. of pure morphine salt were obtained in cubes, m. p. 114—116°. They gave, on decomposition, a hydrogen phthalate (m. p. 50—52°) having $[\alpha]_D$ + 12·6°.

Preparation of Esters.—The *formates* of *d*-ethylvinylcarbinol and of *d*-n-butylvinylcarbinol were prepared by heating the alcohols at 100° with a slight excess of anhydrous formic acid, the *acetates* of *d*-ethylvinylcarbinol and of *l*-n-butylvinylcarbinol and the n-*butyrate* of *d*-n-butylvinylcarbinol by the interaction of the alcohols and the requisite acid anhydride, and the *benzoate* of *d*-n-butylvinylcarbinol by the interaction of benzoyl chloride and the alcohol in pyridine solution. Each of the esters was redistilled until its refractive index was constant. The formate and the n-butyrate of *d*-n-butylvinylcarbinol were hydrolysed; the alcohol recovered in each case was of full rotatory power.

The b. p.'s (at 760 mm.) of the esters are as follows. Ethylvinylcarbinol : formate, 115·5—116·5°; acetate, 126·5—127·5°. n-Butylvinylcarbinol : formate, 155—157°; acetate, 165—167°; n-butyrate, 198—200°; benzoate, 152—153° (18 mm.).

Reduction of l-n-*Butylvinylcarbinol.*—The method first tried, in which platinum black was used as a catalyst (Vavon, *Ann. Chim.*, 1914, **1**, 144), was unsuccessful; the unsaturated alcohol was recovered unchanged after 48 hours' shaking in an atmosphere of hydrogen. Similarly, the hydrogen phthalate of the *l*-carbinol was recovered unchanged after prolonged shaking in an atmosphere of

Rotatory Powers of the Carbinols in the Homogeneous State at 20°.

Length of Observation Tubes—200 mm. for visual, 100 mm. for photographic readings.

λ.	d-Methylvinylcarbinol.		d-Ethylvinylcarbinol.		l-n-Propylvinylcarbinol.		l-n-Butylvinylcarbinol.	
	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.
Visual readings.								
6708	+40·97°	25·00°	+43·69°	+25·98°	−35·60°	−21·22°	−32·36°	−19·31°
5893	55·67	33·89	59·16	35·20	48·52	28·92	43·94	26·20
5790	58·86	35·13	62·04	36·90	50·30	29·86	45·71	27·27
5461	67·17	40·38	71·36	42·44	57·62	34·55	52·85	31·53
4359	121·02	72·39	129·25	76·88	105·62	62·70	95·77	57·39
Photographic readings.								
4816	61·99	74·39	—	—	56·38	67·20	49·46	59·16
4272	—	—	75	89·2	61·18	72·96	50·88	60·81
4144	—	—	—	—	64·18	76·54	53·38	66·56
4077	72·99	87·46	—	—	67·88	80·91	59·18	70·06
4005	—	—	—	—	69·18	82·44	62·08	74·08
3979	78·49	94·13	—	—	—	—	62·88	74·92
3923	81·99	98·23	—	—	—	—	—	—
3830	—	—	95	113	—	—	—	—
$D^{20°}_{4°}$	0·8320		0·8406		0·8370		0·8360	

Rotatory Powers of the Esters in the Homogeneous State at 20°.

λ.	d-n-Butylvinyl-carbinyl formate. l = 100 mm.		l-n-Butylvinyl-carbinyl acetate. l = 100 mm.		d-n-Butylvinyl-carbinyl n-butyrate. l = 100 mm.		d-n-Butylvinyl-carbinyl benzoate. l = 100 mm.	
	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.
6708	−12·25°	−13·99°	+2·74°	+3·16°	−1·83°	−2·11°	+30·41°	+30·30°
5893	15·61	17·83	3·78	4·36	2·50	2·88	41·60	41·47
5790	16·37	18·70	4·27	4·93	3·31	3·81	44·05	43·91
5461	20·18	23·05	4·54	5·23	3·47	3·99	51·43	51·26
4359	35·72	40·80	8·27	9·53	5·38	6·19	99·94	99·63
$D^{20°}_{4°}$	0·8754		0·8682		0·8696		1·0033	

λ.	d-Ethylvinyl-carbinyl acetate. l = 50 mm.		d-Ethylvinyl-carbinyl formate. l = 25 mm.	
	α_λ.	$[\alpha]_\lambda$.	α_λ.	$[\alpha]_\lambda$.
6708	−3·61	−8·48°	−5·94°	−26·59°
5893	4·78	11·14	7·75	34·69
5790	5·14	12·02	8·28	37·03
5461	5·90	13·82	9·43	42·17
4359	10·14	23·64	16·69	74·64
$D^{20°}_{4°}$	0·8733		0·8953	

Alcohols.

Observed rotations in a 50-mm. jacketed tube at different temperatures.

d-*Methylvinylcarbinol.*

λ = 6708 + 10·40° at 21·2°;   9·35° at 38°; 8·08° at 58·5°; 7·40° at 80°
λ = 5893   13·80° at 21·2°; 12·54° at 38°; 10·81° at 59°; 9·26° at 75°.
λ = 5790   14·37° at 21·2°; 12·88° at 39°; 11·66° at 61°; 9·97° at 86°.
λ = 5461   16·51° at 21·2°; 14·92° at 39·5°; 13·33° at 61°; 10·77° at 86·5°.
λ = 4359   29·38° at 21·2°; 26·66° at 39°; 23·60° at 57°; 20·74° at 90·5°.

d-*Ethylvinylcarbinol.*

λ = 6708 +10·92° at 20°; 9·57° at 46°; 8·27° at 71°; 7·87° at 88°; 7·50°
           at 102°.
λ = 5893   14·79° at 20°; 12·86° at 48°; 11·80° at 68°; 10·74° ʼat 88°;
           10·23° at 100·5°.
λ = 5790   15·51° at 20°; 13·20° at 48·6°; 12·13° at 66·5°; 11·18° at 89°;
           10·46° at 104°.
λ = 5461   17·84° at 20°; 15·36° at 48·3°; 14·04° at 67°; 12·83° at 89·5°;
           12·22° at 103·8°.
λ = 4359   32·30° at 20°; 28·43° at 47·2°; 25·76° at 67°; 23·69° at 88·1°;
           23·00° at 98·6°.

l-n-*Propylvinylcarbinol.*

λ = 6708 —8·62° at 21·5°; 7·24° at 42°; 6·46° at 61°; 5·00° at 97°; 4·38°
           at 109°.
λ = 5893   11·56° at 21·5°; 9·16° at 43·5°; 8·90° at 64°; 6·44° at 97°;
           6·16° at 109°.
λ = 5790   12·08° at 21·5°; 10·46° at 46·5°; 9·50° at 62°; 6·92° at 99°;
           6·52° at 109°.
λ = 5461   14·03° at 21·5°; 11·86° at 47°; 10·82° at 63°; 8·06° at 99°;
           7·50° at 109°.
λ = 4359   25·68° at 21·5°; 22·03° at 46°; 19·64° at 61·5°; 14·21° at 100°;
           13·01° at 109°.

l-n-*Butylvinylcarbinol.*

λ = 6708 —7·58° at 20·5°; 6·00° at 52°; 4·61° at 85°; 3·78° at 108°; 3·40°
           at 128°.
λ = 5893   10·27° at 20·5°; 8·94° at 53°; 6·10° at 85°; 5·16° at 108°; 4·36°
           at 130°.
λ = 5790   10·90° at 20·5°; 8·89° at 52°; 7·00° at 82·5°; 5·68° at 108°;
           5·09° at 129°.
λ = 5461   12·65° at 20·5°; 10·20° at 52°; 8·01° at 82·5°; 6·51° at 109·5°;
           5·85° at 128°.
λ = 4359   23·07° at 20·5°; 18·63° at 52·5°; 15·32° at 82·5°; 12·52° at 108°;
           11·35° at 129°.

Ester.

d-*Ethylvinylcarbinyl acetate.*

λ = 6708 —3·61° at 20°; 4·21° at 41°; 4·65° at 71°; 4·70° at 96°; 4·75°
           at 107°.
λ = 5893   4·78° at 20°; 5·45° at 44°; 5·72° at 72°; 5·90° at 98°; 5·95°
           at 107°.
λ = 5790   5·14° at 20°; 6·20° at 44°; 6·75° at 72°; 6·95° at 96°; 7·00°
           at 107°.
λ = 5461   5·90° at 20°; 7·10° at 42°; 7·82° at 71°; 7·91° at 97°; 7·96°
           at 105°.
λ = 4359   10·14° at 20°; 11·80° at 48°; 12·30° at 71°; 12·35° at 74°;
           12·48° at 90°; 12·60° at 107°.

Specific Rotatory Powers of the Alcohols in Various Solvents.
Temperature 18—20°.   l = 200 mm.

Alcohol.	Solvent.	Grams of solute in 100 c.c. of solution.	$[\alpha]_\lambda$							
			Visual.					Photographic.		
			6708.	5893.	5790.	5461.	4359.	4077.	4005.	3979.
d-Ethylvinylcarbinol	Ethyl alcohol	5·125	+21·46°	+34·34°	+35·02°	+41·56°	+77·18°	—	—	—
,,	Carbon disulphide	4·867	26·83	36·67	37·90	43·25	78·07	—	—	—
,,	Benzene	5·1215	23·86	30·76	31·83	36·30	67·78	—	—	—
l-n-Butylvinylcarbinol	Ethyl alcohol	4·695	−18·50	−22·58	−24·50	−28·22	−50·61	—	—	—
,,	Carbon disulphide	4·915	−18·46	−22·38	−22·79	−27·26	−50·05	—	—	—
,,	cycloHexane	23·985	−19·83	−26·75	−28·06	−32·33	−58·70	−71·5	−75·5	−76·7

Refractive Indices, $n_\lambda^{20°}$.

	Carbinols of the formula CH₂:CH·CH(OH)·R.				d-Ethylvinylcarbinyl		Esters. n-Butylvinylcarbinyl			
λ.	Me.	Et.	Pr.	Bu.	formate.	acetate.	formate.	acetate.	n-butyrate.	benzoate.
6708	·4100	1·4192	1·4248	1·4310	1·4074	1·4080	1·4193	1·4164	1·4221	1·4990
6402	·4103	1·4201	1·4251	1·4314	1·4079	1·4095	1·4199	1·4182	1·4225	1·4993
6096	·4115	1·4209	1·4261	1·4324	1·4092	1·4108	1·4202	1·4191	1·4236	1·5004
5896	·4120	1·4218	1·4268	1·4337	1·4104	1·4115	1·4225	1·4200	1·4241	1·5038
5882	·4118	1·4223	1·4270	1·4334	1·4097	1·4112	1·4227	1·4198	1·4242	1·5038
5790	·4126	1·4227	1·4283	1·4340	1·4102	1·4121	1·4229	1·4199	1·4243	1·5039
5782	·4126	1·4226	1·4275	1·4339	1·4105	1·4121	1·4228	1·4203	1·4243	1·5039
5700	·4128	1·4232	1·4278	1·4341	1·4109	1·4124	1·4231	1·4208	1·4245	1·5040
5461	·4144	1·4245	1·4296	1·4361	1·4119	1·4137	1·4245	1·4232	1·4261	1·5081
5218	·4157	1·4256	1·4305	1·4373	1·4134	1·4149	1·4249	1·4237	1·4270	1·5082
5153	·4162	1·4264	1·4311	1·4377	1·4140	1·4153	1·4263	1·4239	1·4273	1·5091
5106	·4165	1·4265	1·4315	1·4378	1·4144	1·4156	1·4257	1·4241	1·4272	1·5097
4359	·4235	1·4339	1·4339	1·4457	1·4208	1·4222	1·4340	1·4355	1·4263	1·5253

Densities.

All determinations of density were carried out with a pyknometer of about 1·5 c.c. capacity.

d-*Methylvinylcarbinol.* D_4^t 0·8362 at 15·5°, 0·8156 at 39°, 0·7979 at 59·5°, 0·7746 at 84°.

d-*Ethylvinylcarbinol.* 0·8404 at 20·5°, 0·8200 at 42·8°, 0·8021 at 60·8°, 0·7890 at 76·2°, 0·7764 at 88·2°.

l-n-*Propylvinylcarbinol.* 0·8403 at 15°, 0·8186 at 42°, 0·7928 at 68·5°, 0·7656 at 94°, 0·7432 at 120°.

d-n-*Butylvinylcarbinol.* 0·8345 at 22·8°, 0·8144 at 49°, 0·7918 at 73·5°, 0·7628 at 110°, 0·7528 at 121°.

d-*Ethylvinylcarbinyl formate.* 0·8902 at 25·5°, 0·8699 at 46·5°, 0·8514 at 65°, 0·8242 at 94°, 0·8157 at 102°.

d-*Ethylvinylcarbinyl acetate.* 0·8805 at 22·1°, 0·8626 at 31·6°, 0·8521 at 54°, 0·8291 at 73·5°, 0·8085 at 88°, 0·7975 at 100·5°.

$$D_{4°}^{20°}.$$

d-n-Butylvinylcarbinyl	formate	0·8754
,, ,, ,,	acetate	0·8682
,, ,, ,,	*n*-butyrate	0·8696
,, ,, ,,	benzoate	1·0033

hydrogen. The second method, due to Skita (*Ber.*, 1912, **45**, 3589), was completely successful; the calculated quantity of hydrogen was absorbed within 2½ hours. After the physical constants of the *l*-butylethylcarbinol had been determined, the alcohol was converted into its hydrogen phthalate by the ordinary method and the constants of this crystalline compound were determined. Thus the identity of the reduced alcohol was completely established. In a further experiment *l*-n-butylvinylcarbinyl acetate, which had [α]$_D$ + 4·36°, was reduced by Skita's method; on account of the difficulty of isolating the reduced ester without some hydrolysis taking place (owing to acetic acid being used as solvent), its complete hydrolysis was effected, and the product isolated as the reduced alcohol, the rotatory power of which was identical with that of the alcohol obtained by the reduction of the unsaturated alcohol.

CLXIII.—*A Synthesis of Pyrylium Salts of Antho-*
cyanidin Type. Part VII. The Preparation of
the Anthocyanidins with the Aid of 2 : 4 : 6-Tri-
acetoxybenzaldehyde.

By DAVID DOIG PRATT and ROBERT ROBINSON.

HAVING completed the task of the synthesis of the three funda-
mental anthocyanidins and of the pyrylium salts most closely
related to the more important naturally occurring flavones and
flavonols, we have turned our attention to improvements of method,
especially such as would render feasible the synthesis of the methyl
ethers of cyanidin and delphinidin, e.g., peonidin, oenidin, or
myrtillidin. Demethylation with hydriodic acid, employed as the
final stage in every previous case, is obviously inadmissible and
either the hydroxyl and methoxyl groups must be present in the
components as such in the desired positions, or the former must
be protected by groups, such as acetyl or carbomethoxy, which can
be readily removed by acid hydrolysis under moderate conditions.
Since most of the natural methylated anthocyanidins contain
hydroxyl groups in positions 5 and 7 in the phloroglucinol nucleus,
it was of primary importance to devise a method whereby phloro-
glucinaldehyde could be employed in syntheses of the type which
we are developing. Owing to the high reactivity displayed by this
substance and its great tendency to pass into red insoluble products
in presence of mineral acid our experience of the direct process
was most discouraging. If, however, the nuclear reactivity of the
aldehyde is depressed by acetylating all the hydroxyl groups and
the condensations are carried out in absolute formic * acid solution,
satisfactory results are obtained and the method constitutes by far
the most convenient process for the preparation of the antho-
cyanidins.

    2 : 4 : 6-*Triacetoxybenzaldehyde* (I) reacts with ω-methoxyaceto-
phenone derivatives in presence of hydrogen chloride in accordance
with the scheme :

* The use of 80% formic acid as a solvent in condensations to pyrylium
salts was introduced by Buck and Heilbron (J., 1922, **121**, 1199) and in our
experience tends to increase yields. The very numerous syntheses of this
class described as occurring in acetic acid solution would no doubt in the
majority of cases proceed more satisfactorily in the new medium. In the
reactions described in this communication we employ absolute formic acid
in order to avoid premature hydrolysis of the acetyl groups, and the first
appearance of intense colour after the introduction of hydrogen chloride
usually synchronises with the evolution of carbon monoxide.

$$\underset{\underset{\text{AcO}}{\text{AcO}}}{\text{AcO}}\Big\langle\underset{\text{CHO}}{\text{OAc}}\ +\ \underset{\underset{\text{CH}_2\cdot\text{OMe}}{|}}{\text{CO}}\!\!-\!\!\!\!\!\!<\ \xrightarrow{\text{HCl}}\ \underset{\text{AcO}}{\text{AcO}}\Big\langle\!\!\overset{\overset{\text{Cl}}{\frown}}{\underset{O}{}}\Big\rangle\!\!\overset{}{\underset{\text{OMe}}{}}\!\!<\ +\text{AcOH}+\text{H}_2\text{O}$$

(I.)
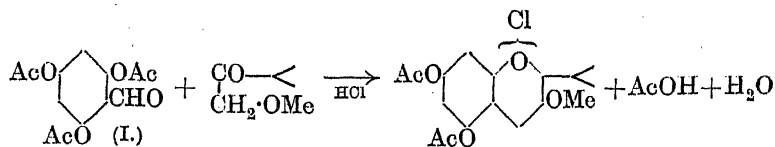
The salt precipitated from the reaction mixture by ether is hydrolysed by boiling aqueous alcoholic hydrochloric acid. In this way, using the ketonic components previously coupled with 2-hydroxy-4 : 6-dimethoxybenzaldehyde, we have prepared pelargonidin chloride 3 : 4'-dimethyl ether, cyanidin chloride 3 : 3' : 4'-trimethyl ether, morinidin chloride 3 : 2' : 4'-trimethyl ether, and delphinidin chloride 3 : 3' : 4' : 5'-tetramethyl ether. On demethylation of these salts by the usual series of processes pelargonidin, cyanidin, morinidin and delphinidin salts, respectively, were obtained. Two new isomerides of pelargonidin have been synthesised. o-Methoxybenzoyl chloride and m-methoxybenzoyl chloride react with ethyl sodio-αγ-dimethoxyacetoacetate in ethereal solution to give products which yield ω : 2-dimethoxyacetophenone (II) and ω : 3-dimethoxyacetophenone (III), respectively, on hydrolysis. These ketones yield, on condensation with 2 : 4 : 6-

$$\text{(II.)}\quad \Big\langle\ \Big\rangle\!\!\underset{\text{CO}\cdot\text{CH}_2\cdot\text{OMe}}{\overset{\text{OMe}}{}}\qquad\qquad \text{MeO}\Big\langle\ \Big\rangle\text{CO}\cdot\text{CH}_2\cdot\text{OMe}\quad\text{(III.)}$$
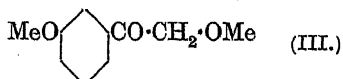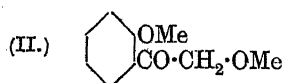
triacetoxybenzaldehyde, hydrolysis, and demethylation of the products, 3 : 5 : 7 : 2'-tetrahydroxyflavylium chloride (IV) and 3 : 5 : 7 : 3'-tetrahydroxyflavylium chloride (V). The former is related to the flavonol datiscetin and is therefore termed *datiscetinidin chloride*.

$$\text{(IV.)}\ \ \underset{\text{HO}}{\text{HO}}\Big\langle\!\!\overset{\overset{\text{Cl}}{\frown}}{\underset{O}{}}\Big\rangle\!\!\underset{\text{OH}}{}\!\overset{\text{HO}}{}\Big\langle\ \Big\rangle \qquad\qquad \underset{\text{HO}}{\text{HO}}\Big\langle\!\!\overset{\overset{\text{Cl}}{\frown}}{\underset{O}{}}\Big\rangle\!\!\underset{\text{OH}}{}\!\overset{\text{OH}}{}\Big\langle\ \Big\rangle\ \text{(V.)}$$
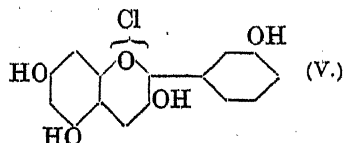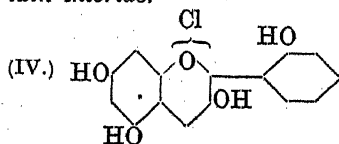
It is of interest to compare the behaviour of these salts with that of pelargonidin chloride. The details of the colour reactions will be found in the experimental section, but a striking experiment may be mentioned here. An alcoholic solution of each salt is diluted with much water. The colour base of datiscetinidin is at once precipitated, the solution of (V) is decolorised, owing to pseudo-base formation, in a very short time, whilst the pelargonidin solution remains clear and dark brownish-red. In time, the pelargonidin solution also deposits some colour-base and pseudo-base remains in solution.

We have not yet discovered satisfactory conditions for the condensation of 2 : 4 : 6-triacetoxybenzaldehyde with ketones, R·COMe, and the method is, for example, not applicable to the preparation of luteolinidin, at least in its present form.

<div align="center">EXPERIMENTAL.</div>

2 : 4 : 6-*Triacetoxybenzaldehyde* (I).—Acetic anhydride (50 c.c.) was added to a mixture of phloroglucinaldehyde (10 g.) and potassium carbonate (10 g.), when considerable heat was evolved, and on subsidence of the reaction a further portion of potassium carbonate (5 g.) was introduced. The mass was well stirred and after an hour water was added and the precipitate collected, washed, drained, and heated to boiling with methyl alcohol (50 c.c.). The derivative, which separated in prisms on cooling, was washed with a little methyl alcohol and dried in air (yield 12·5—14 g.). This product is almost pure and can be employed for most purposes. The substance crystallises from methyl alcohol in colourless, hexagonal prisms, m. p. 151° (Found, in material dried in a vacuum over sulphuric acid : C, 54·0; H, 4·6; in material dried at 100° : C, 54·1; H, 4·6. $C_{13}H_{12}O_7,0.5H_2O$ requires C, 54·0; H, 4·5%). Prolonged heating above 100° causes some decomposition and we have no evidence regarding the mode of combination of the attached water. This may well be constitutional and some such arrangement as the following is possible :

$$\text{CMe·OH} \qquad \text{CMe·OH}$$

$$\begin{array}{ccccc} \text{O} & \text{O} & & \text{O} & \text{O} \\ & & \text{CH—O—CH} & & \\ \wedge & & & & \wedge \end{array}$$
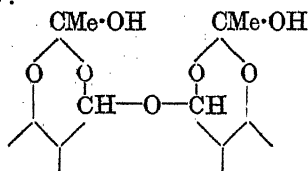
The substance is insoluble in cold dilute aqueous sodium hydroxide and gives no coloration with ferric chloride in alcoholic solution.

ω : 2-*Dimethoxyacetophenone* (II).—Ethyl αγ-dimethoxyacetoacetate * (29·5 g.) was converted into its sodio-derivative by means of granulated sodium (3·6 g.) in ethereal suspension, and o-methoxybenzoyl chloride (25·5 g.) then added to the mixture which, after subsidence of the initial gentle reaction, was heated on the steam-bath under reflux for 4 hours. The neutral product was isolated (42 g.) and hydrolysed by aqueous potassium hydroxide (900 c.c. of 2·5%), first in the cold by agitation for 12 hours and then at the boiling point for 4 hours. The cooled liquid was saturated with potassium carbonate and extracted with ether. The ketone (12 g.),

* The proportion of sodium used in the preparation of this substance from ethyl methoxyacetate, previously suggested (this vol., p. 168) can advantageously be increased by 50%.

b. p. 165°/15 mm., was isolated in the usual manner (Found: C, 66·7; H, 6·7. $C_{10}H_{12}O_3$ requires C, 66·7; H, 6·7%). The oil could not be induced to crystallise and yielded a *semicarbazone* crystallising from water in clusters of jagged needles, m. p. 137°.

In an entirely similar manner, ethyl αγ-dimethoxyacetoacetate (36 g.) and *m*-methoxybenzoyl chloride (32 g.) gave rise to 12·5 g. of a pale yellow oil consisting of ω : 3-*dimethoxyacetophenone* (III), b. p. 155°/18 mm. (Found: C, 66·8; H, 6·6%). The *semicarbazone* crystallises from aqueous alcohol in clusters of colourless needles, m. p. 128°.

Datiscetinidin Chloride 3 : 2′-*Dimethyl Ether* (corresponding with IV).—Hydrogen chloride was passed for 2 hours through a mixture of ω : 2-dimethoxyacetophenone (3·1 g.), 2 : 4 : 6-triacetoxybenz-aldehyde (5 g.), and formic acid (15 c.c.). After 12 hours, a con-siderable crystallisation of a bright red substance had occurred and after the addition of a large volume of ether the solid was collected and added to ethyl alcohol (500 c.c.) containing concentrated hydro-chloric acid (10 c.c.). On boiling, the salt did not pass completely into solution. The mixture was heated under reflux for 1·5 hours, concentrated hydrochloric acid (40 c.c.) added, and the alcohol removed as far as possible by distillation from the steam-bath. Water was added and the solid collected and washed with 0·5% hydrochloric acid. The well-drained material was added to boiling water (750 c.c.) and hydrochloric acid (10 c.c. of 10%) and precipi-tated from the filtered solution in slender, orange-red needles (3 g.) by the addition of 20% hydrochloric acid (100 c.c.) (Found, in material dried in a vacuum : C, 60·6; H, 4·5. $C_{17}H_{15}O_5Cl$ requires C, 60·9; H, 4·5%). This salt is characterised by its extremely sparing solubility even in hot dilute hydrochloric acid and by its orange-red colour. It darkens at 250°, but does not melt at 280°.

Datiscetinidin Chloride (IV).—A mixture of dimethyldatiscetinidin chloride (2 g.), phenol (6 g.), and hydriodic acid (50 c.c.; *d* 1·7) was gently boiled in a stream of carbon dioxide for 30 minutes; on cooling, the demethylated iodide crystallised in slender, red needles. These (1 g.) were dissolved in alcohol (20 c.c.) containing a trace of hydrogen chloride and an excess of silver chloride, and the mixture was heated gently for 15 minutes. Hydrochloric acid (20 c.c. of 12%) was added to the filtered solution, and the chloride then separated in fine, red needles which darkened at 240° (Found, in material dried in a vacuum over sulphuric acid : C, 55·3; H, 4·3. $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·5; H, 4·0%). This salt is very sparingly soluble in dilute hydrochloric acid, and the colour of its solutions in the simple alcohols is red, bluer than that of galanginidin but not so blue nor so intensely coloured as a solution of pelar-

gonidin of similar concentration. In alcoholic solution, a trace of
sodium carbonate gives a violet coloration, which, on the addition
of more sodium carbonate, becomes at once more intense and duller
in tone, whilst on dilution with water the colour is reddish-violet.
The reactions are the same when sodium hydroxide is employed.
The formation of pseudo-base and of colour-base was observed,
but, as in the case of morinidin, the former appears to undergo
further change in solution.

5 : 7-*Dihydroxy*-3 : 3'-*dimethoxyflavylium Chloride* (corresponding
with V).—The condensation of ω : 3-dimethoxyacetophenone (6·2 g.)
with 2 : 4 : 6-triacetoxybenzaldehyde (10 g.) in formic acid (40 c.c.)
solution by means of hydrogen chloride was carried out in 3 hours.
The product, precipitated by ether, was dissolved in alcohol (300 c.c.),
to which concentrated hydrochloric acid (50 c.c.) was later added.
The solution was boiled for 15 minutes and the alcohol removed
by distillation from the steam-bath and finally by evaporation in
a vacuum. The crystalline precipitate was washed with 0·5%
hydrochloric acid, dissolved in 400 c.c. of hot 0·5% hydrochloric acid,
and the solution filtered. The addition of 10% hydrochloric acid
(200 c.c.) caused deep brownish-crimson clusters of microscopic
needles to separate, even from the hot solution. Further quantities
could be obtained from the original mother-liquor and from the
residue, and the total yield was 6·8 g. (Found, in material dried in a
vacuum over sulphuric acid : C, 57·9; H, 5·0. $C_{17}H_{15}O_5Cl,H_2O$
requires C, 57·8; H, 4·8%).

The salt darkens at 195° and decomposes at 225°. The substance
is much more readily soluble in alcohol than the isomerides described
in this communication, and when the cherry-red solution is largely
diluted with water complete decoloration is rapid. The orange-
red colour of the oxonium salt is quantitatively restored by the
addition of hydrochloric acid.

3 : 5 : 7 : 3'-*Tetrahydroxyflavylium Chloride* (V).—The salt last
described (3 g.) was demethylated by boiling hydriodic acid (80 c.c.;
d 1·7) in presence of phenol (15 g.) during 30 minutes. After cooling,
the red, prismatic needles were collected (1·8 g.) and washed with
ether. Conversion into the chloride was carried out in ethyl alcohol
(30 c.c.) and the filtered solution was mixed with hydrochloric acid
(30 c.c. of 6%). The chloride separated in prismatic needles and
was recrystallised from hot 6% hydrochloric acid (Found, in material
dried in a vacuum over sulphuric acid : C, 55·8; H, 4·2.
$C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·5; H, 4·0%). The salt decomposes
at 200°. Its acid alcoholic solutions resemble those of pelargonidin,
but the tone is duller and browner. The substance is more soluble
in dilute hydrochloric acid than datiscetinidin or pelargonidin

chloride and it is distinguished from its isomerides by a remarkable faculty for passing into the pseudo-base. Aqueous alkaline solutions are reddish-violet, whilst in alcoholic solution a curiously dichroic reddish-blue colour is produced by addition of a trace of sodium hydroxide or excess of sodium carbonate. A trace of sodium carbonate gives a violet solution. This salt and also datiscetinidin chloride, like pelargonidin chloride, reduces Fehling's solution and is extracted from aqueous solution by *iso*amyl alcohol.

Pelargonidin Chloride 3 : 3′-*Dimethyl Ether*.—Hydrogen chloride was led for 2 hours through a solution of ω : 4-dimethoxyacetophenone (5·4 g.) and 2 : 4 : 6-triacetoxybenzaldehyde (8 g.) in absolute formic acid (25 c.c.). The deep crimson product was precipitated by the addition of much ether and dissolved as far as possible in boiling ethyl alcohol, to which concentrated hydrochloric acid (50 c.c.) was added. The mixture was boiled for 10 minutes, diluted with an equal volume of water, and, after cooling, the solid was collected. The oxonium salt was then isolated by extraction with boiling water containing a little hydrochloric acid (about 0·1%). On addition of concentrated hydrochloric acid to the filtrates, the very sparingly soluble dimethylpelargonidin chloride separated completely, and to a large extent from the hot liquid, in intense crimson rosettes and sheaves of glistening, microscopic needles (6·5 g.). The salt was recrystallised from 0·5% hydrochloric acid (Found, in material dried in a vacuum : C, 61·1; H, 4·8. $C_{17}H_{15}O_5Cl$ requires C, 60·9; H, 4·5%). The substance also crystallises in squat prisms; it does not melt at 300°. Its orange solution in sulphuric acid exhibits a green fluorescence. The colour of an acid alcoholic solution resembles that of pelargonidin, but is rather less bluish-red in tinge. When the crystals are covered with distilled water, a portion dissolves to a pinkish-yellow solution which very soon becomes colourless. On heating with distilled water a deep orange solution is obtained and this also becomes colourless on great dilution. Also the orange solution treated with sodium acetate gives a dull brownish-violet colour-base which rapidly passes into colourless solution. All these decolorised solutions contain the pseudo-base and become orange on the addition of hydrochloric acid. On shaking an aqueous solution with *iso*amyl alcohol, the colour passes completely to the latter. The intense cherry-red extract with aqueous sodium carbonate gives a yellow watery layer and a pale purplish-brown alcoholic layer.

Pelargonidin Chloride.—Demethylation of the dimethyl ether (3 g.) was carried out during 30 minutes by means of a gently boiling mixture of hydriodic acid (100 c.c.; *d* 1·7) and phenol (10 g.). On cooling, the iodide (3·1 g.) separated in glistening, rectangular

prisms. The supposed pelargonidin chloride obtained from this persisted in crystallising in highly characteristic, diamond-shaped plates, and as pelargonidin chloride has never been observed to separate in this form we concluded that the specimen was contaminated with methylated material; the sodium carbonate reaction was also purple rather than blue. The substance was therefore again demethylated, relatively twice as much phenol being used. The recovered iodide was converted into chloride and this was identical in every respect with pelargonidin chloride. The colour of acid solutions, the form of the crystals obtained under different conditions of crystallisation, the blue colour in sodium carbonate solution, the colour-base, the formation of pseudo-base, and the chief absorption band in alcoholic solution were examined.

Morinidin Chloride 3 : 2′ : 4′-*Trimethyl Ether*.—A solution of ω : 2 : 4-trimethoxyacetophenone (5 g.) and 2 : 4 : 6-triacetoxy-benzaldehyde (7 g.) in formic acid (25 c.c.) was saturated with hydrogen chloride during 3 hours, and ether added to the dark red solution until no further precipitation occurred. The viscous material insoluble in ether was well washed with the solvent and dissolved in ethyl alcohol (50 c.c.), and concentrated hydrochloric acid (30 c.c.) added. On boiling, the anthocyanindin-like colour became much intensified and in a few minutes the whole of the salt crystallised from the hot solution. The substance was crystallised from boiling methyl alcohol by the addition of hydrochloric acid to the filtered solution. It separated in brick-red, short, microscopic needles and in a similar form from hot very dilute hydrochloric acid (about 0·5%) (Found, in material dried in a vacuum over sulphuric acid : C, 59·4; H, 4·9. $C_{18}H_{17}O_6Cl$ requires C, 59·3; H, 4·7%). The salt gradually darkens on heating at 250°, but does not melt at 300°. Aqueous solutions of this salt are orange-red; on dilution a crimson colour is obtained and on great dilution, decoloration ensues. The orange colour is restored by the addition of a mineral acid. The colour-base is a dark mauve-crimson precipitate and the solution in aqueous ammonia is blood-red. The red solution in sulphuric acid has a bright green fluorescence. The dry chloride is insoluble in chloroform, but on the addition of a trace of ferric chloride an eosine-red solution is at once produced. The *perchlorate* is extremely sparingly soluble in dilute aqueous perchloric acid and crystallises from alcohol containing a little perchloric acid in slender, microscopic, crimson needles. The trimethylmorinidin chloride (1·8 g.) was mixed with phenol (5 g.) and hydriodic acid (50 c.c.; *d* 1·7), and the mixture boiled for 25 minutes in a neutral atmosphere. On cooling, the iodide separated in hair-fine, red needles (1·8 g.). The related chloride showed all the properties

of morinidin chloride as previously described (this vol., p. 1137; compare Willstätter and Schmidt, *Ber.*, 1924, **57**, 1945). The addition of hydrogen peroxide to the dichroic solution of morinidin chloride in aqueous sodium carbonate gives a brownish-yellow, intensely green, fluorescent solution, but definite products have not yet been isolated from this.

Cyanidin Chloride 3 : 3′ : 4′-*Trimethyl Ether.*—The quantities, times, and method employed in preparing this salt from ω-methoxyacetoveratrone (this vol., p. 170) were the same as those given above in the case of trimethylmorinidin. The hydrolysis of the product was conducted at the boiling point for 15 minutes. The paste obtained on cooling was transferred to the filter with the aid of alcohol (15 c.c.), mixed with concentrated hydrochloric acid (15 c.c.), well drained, and dried (7 g.). The substance was dissolved in hot ethyl alcohol (160 c.c.), and concentrated hydrochloric acid (10 c.c.) added to the filtered solution. The deep crimson solution deposited dense aggregates of small needles (Found, in material dried in a vacuum over sulphuric acid : C, 55·2; H, 5·3. $C_{18}H_{17}O_6Cl,1\cdot5H_2O$ requires C, 55·2; H, 5·1%). This specimen decomposed at 208°. The properties of this salt closely resemble those of dimethylpelargonidin chloride. The red alcoholic solution has a slightly more bluish shade and the salt is more readily soluble in dilute hydrochloric acid. In time, it separates completely from 0·5% hydrochloric acid solution.

Cyanidin Chloride.—A mixture of trimethylcyanidin chloride (3 g.), phenol (6 g.), and hydriodic acid (150 c.c.; d 1·7) was heated to gentle ebullition for 35 minutes in a stream of carbon dioxide. Reddish-brown, prismatic needles separated from the hot solution and, on cooling, the substance was collected, washed with ether, and dried (3 g.). The iodide exhibits a golden lustre and does not melt at 300°. The chloride obtained by double decomposition with silver chloride in the usual manner exhibited the characteristic reactions of cyanidin and was found by careful direct comparison to be identical with the specimen of the anthocyanidin previously synthesised (this vol., p. 172), which had itself been compared with an authentic specimen of natural origin.

Delphinidin Chloride 3 : 3′ : 4′ : 5′-*Tetramethyl Ether.*—Hydrogen chloride was passed through a solution of ω : 3 : 4 : 5-tetramethoxyacetophenone (2·8 g.) (this vol., p. 173) and 2 : 4 : 6-triacetoxybenzaldehyde (3·6 g.) in formic acid (15 c.c.) for 2·5 hours. On the addition of ether the syrupy residue gradually crystallised, the mass exhibiting brown-golden reflex. The washed product dissolved completely in ethyl alcohol (30 c.c.) and after the addition of concentrated hydrochloric acid (15 c.c.) the mixture was boiled

for 20 minutes and cooled. The crystals (1·8 g.) were recrystallised by very slow cooling of a hot solution of the whole in 6% aqueous hydrochloric acid (1200 c.c.). The slender, glistening needles exhibit a dark green reflex and do not melt at 250° (Found, in material dried in a vacuum : C, 53·2; H, 5·6. $C_{19}H_{19}O_7Cl,2H_2O$ requires C, 53·0; H, 5·3%). This substance dissolves in alcohol to a blue cherry-red solution which is rapidly decolorised on dilution with water, the colour being fully restored by addition of mineral acid. Although containing four methoxyl groups, the substance in solution in aqueous sodium carbonate has a greenish-brown tinge, and its solutions do not resemble those of the anthocyanidins. This salt, like all the other 5 : 7-dihydroxyflavylium chlorides here described, is sparingly soluble in dilute hydrochloric acid and exhibits a strong tendency to crystallise.

Delphinidin Chloride.—A mixture of the tetramethyl ether (1 g.), phenol (5 g.), and hydriodic acid (50 c.c.; *d* 1·7) was boiled in an atmosphere of carbon dioxide for 30 minutes. The iodide crystallised, on cooling, in prismatic needles with a golden-green reflex and was isolated (1 g.). After conversion to the chloride, the identity of the salt with delphinidin chloride was established by comparison with the specimen previously synthesised (this vol., p. 174) in respect of the colour in acid solutions, formation of colour-base and pseudo-base, solubility of the salts in 5% hydrochloric acid and 7% sulphuric acid, the ferric chloride reaction in alcohol and in water, and the colours of the solutions in aqueous sodium carbonate. The appearance of the crystals in mass and under the microscope was identical in both cases, and the characteristic hydrate, $C_{15}H_{11}O_7Cl,2H_2O$, was obtained in flat prisms, sparingly soluble in 5% hydrochloric acid and 7% sulphuric acid.

CLXIV.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part VIII. A New Synthesis of Pelargonidin Chloride and of Galanginidin Chloride.*

By THOMAS MALKIN and ROBERT ROBINSON.

Two of the three chief methods available for the preparation of hydroxybenzopyrylium salts having been exploited by Willstätter and his colleagues and by Pratt and Robinson in the synthesis of

the anthocyanidins, we have directed our attention to the third process, that of C. Bülow, in order to determine whether it also is available for this purpose. The first case chosen was that of galanginidin (Willstätter and Schmidt, *Ber.*, 1924, **57**, 1945; Pratt and Robinson, this vol., p. 1135), the 3-methyl ether (II) of which we have prepared by the 2 : 4 : 6-triacetoxybenzaldehyde method (preceding paper) for comparison with the salt obtained according to the scheme :
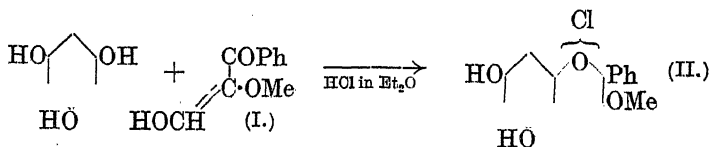
The two substances were identical and the methyl ether was converted into galanginidin chloride by the usual series of processes. The hydroxymethylene derivative (I) of ω-methoxyacetophenone is a crystalline enolic substance obtained without difficulty as its sodium salt by condensation of the ketone with ethyl formate in presence of sodium ethoxide. When ω : 4-dimethoxyacetophenone was condensed with ethyl formate in a similar manner, an oily hydroxymethylene derivative was produced, and this was condensed with phloroglucinol by means of hydrogen chloride to a pelargonidin chloride dimethyl ether, which was very similar to the substance obtained by Pratt and Robinson (preceding paper) from 2 : 4 : 6-triacetoxybenzaldehyde and ω : 4-dimethoxyacetophenone, but crystallised with $1H_2O$ under conditions whereby the latter salt is obtained anhydrous. We saw little sign of heterogeneity of our new product, but have reason to suspect that the substance obtained as described in this communication is mixed with some *epi*pelargonidin dimethyl ether (IV), which might arise in the following manner :
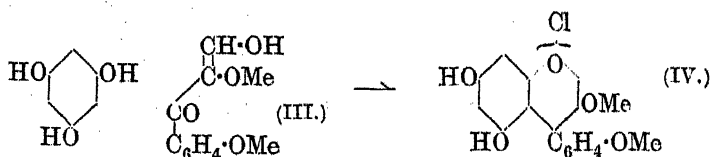
On demethylation and conversion into chloride, a substance was obtained which had the composition and chief properties of pelargonidin chloride, but from which only a small amount of pure pelargonidin chloride of undoubted authenticity could be isolated. The purification was necessarily wasteful and we have no suggestion to offer in regard to the relative amounts of true pelargonidin and pelargonidin-like impurity which were present in the mixture.

We conclude that, on account of the possibility that mixtures may be obtained, the Bülow method is likely to prove an inferior procedure in the synthesis of anthocyanidins.

<div align="center">EXPERIMENTAL.</div>

Phenyl α-Methoxy-β-hydroxyvinyl Ketone (I).—A mixture of ω-methoxyacetophenone (10 g.) and ethyl formate (6 g.) was gradually added with cooling in melting ice to a suspension of sodium ethoxide (4·5 g.) in anhydrous ether (25 c.c.). The orange sodium salt which had separated after 12 hours was washed with ether, dissolved in water at 0°, and mixed with an excess of a cold saturated aqueous solution of copper acetate to which a few drops of acetic acid had been added. The copper derivative was collected, washed with water and ether, and dried. A further quantity could be recovered by shaking the ethereal filtrate from the sodium salt with aqueous copper acetate, thus bringing the total yield to 6 g. The substance could not be recrystallised, but a good specimen melted at 178° (Found : C, 57·4; H, 4·6. $C_{20}H_{18}O_6Cu$ requires C, 57·5; H, 4·3%). When this copper salt (4 g.) was decomposed with 5% sulphuric acid in presence of ether, and the ethereal solution was washed with water and evaporated to a small bulk, the free hydroxymethylene ketone (3 g.) separated in the crystalline condition. The substance crystallises from ether in almost colourless, elongated prisms, m. p. 112° (Found : C, 67·4; H, 5·5. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). In alcoholic solution, the compound gives a brownish-purple coloration with ferric chloride.

Galanginidin Chloride 3-Methyl Ether (II).—(A). Hydrogen chloride was passed for 3 hours through a solution of 2 : 4 : 6-triacetoxybenzaldehyde (11·6 g.) and ω-methoxyacetophenone (6 g.) in absolute formic acid (30 c.c.). After 12 hours, the oxonium salt was precipitated by the addition of much ether, collected, dissolved in methyl alcohol (480 c.c.), and hydrolysed by boiling with concentrated hydrochloric acid (30 c.c.) for ½ hour. Concentrated hydrochloric acid (90 c.c.) was then added and, after half the alcohol had been removed by distillation, 6·5 g. of product crystallised on cooling and 1·0 g. was obtained from the mother-liquor. The substance was recrystallised by solution in hot hydrochloric acid (less than 0·5%), sufficient concentrated acid being added to the filtered liquid to bring the concentration to 5% (Found, in material dried in a vacuum over sulphuric acid : C, 59·5; H, 4·8. $C_{16}H_{13}O_4Cl,H_2O$ requires C, 59·5; H, 4·7%).

(B). Hydrogen chloride was led for 1 hour through a solution of phenyl α-methoxy-β-hydroxyvinyl ketone (0·7 g.) and phloroglucinol (0·49 g.) in dry ether (25 c.c.). After a few hours the dark crimson

crystalline precipitate was collected (0·7 g.) and crystallised as
under (A) (Found : C, 59·5; H, 4·6%). Careful comparison showed
that the substances obtained by these two methods are identical.
In mass the substance is brownish-crimson, but the elongated,
almost rectangular plates are deep orange-brown by transmitted
light. Both specimens crystallised (under conditions which could
not be definitely ascertained) in curved, frond-like aggregates.
The salt is sparingly soluble in cold water and, on boiling, an orange
solution containing much pseudo-base is obtained. In dilute
hydrochloric acid, the salt is very sparingly soluble and on great
dilution, decoloration occurs, the colour being restored by the
addition of acid. Amyl alcohol extracts the salt completely from
aqueous solution, and the colour of the red alcoholic solution is
almost completely discharged on the addition of sodium carbonate.
The tendency of the substance to form pseudo-base in neutral or
alkaline solution is very marked. On the addition of sodium
acetate to an acid solution a deep mauve precipitate of colour base
is obtained, but on dilution this dissolves to a colourless solution.
The *perchlorate* was prepared from specimens made by methods (A)
and (B) and identical results were obtained. The derivative is thrown
down from aqueous solutions in long, fine needles. It crystallises
from glacial acetic acid (0·1 g. in 15 c.c.) in deep brown, flat, elon-
gated, rectangular prisms having a golden reflex. It does not melt
below 300°, but chars slightly at 255—260°.

Galanginidin Chloride.—This salt can best be obtained by
demethylation of its 3-methyl ether prepared by method (A) above.
The chloride (4 g.), phenol (24 g.), and hydriodic acid (100 c.c.;
d 1·7) were heated at 150° in a stream of carbon dioxide for 35
minutes. On cooling, 1·0 g. of iodide crystallised, and a further
1·5 g. was obtained after mixing the filtrate with an equal volume
of ether. The conversion to chloride was carried out by heating
in methyl alcohol (50 c.c.) with precipitated silver chloride (5 g.)
on the steam-bath for 20 minutes, and, on the addition of hot 5%
hydrochloric acid (70 c.c.) to the filtrate, crystallisation of 1·5 g.
occurred immediately. Elongated prisms were obtained by recrystal-
lisation from 3·5% hydrochloric acid, 1·2 g. being dissolved in 300 c.c.
of boiling, very dilute acid and 25 c.c. of concentrated acid added.
(Found, in material dried to constant weight in a vacuum over
sulphuric acid : C, 60·5; H, 4·2. $C_{15}H_{11}O_4Cl,0·5H_2O$ requires
C, 60·1; H, 4·0%). The substance exhibited the reactions described
by Willstätter and Schmidt (*loc. cit.*) and by Pratt and Robinson
(*loc. cit.*). The former authors describe large, air-dried prisms
containing $4H_2O$, and microscopic crystals, containing $2H_2O$, which
lost $1H_2O$ in a vacuum desiccator. Pratt and Robinson found

$2H_2O$ after short drying in a desiccator. These observations are not necessarily inconsistent. The reactions of the salt were similar to those previously recorded.

Anisyl α-Methoxy-β-hydroxyvinyl Ketone (III).—A solution of ω : 4-dimethoxyacetophenone (10 g.) and ethyl formate (4·8 g.) in anhydrous ether (30 c.c.) was slowly added to a suspension of sodium ethoxide (3·8 g.) in ether (30 c.c.), cooled in melting ice. The sodium salt of the hydroxymethylene derivative slowly separated from the red solution and after several hours the mixture was agitated with an equal volume of ice-cold water and the separated aqueous layer treated with a saturated solution of copper acetate. The precipitated salt was washed and dried (13 g.). The substance crystallises from toluene in pale green, microscopic needles, sintering at 163° and melting at 170° (Found : C, 55·3 ; H, 4·7. $C_{22}H_{22}O_8Cu$ requires C, 55·3 ; H, 4·6%). The free enol was obtained in the usual manner by means of dilute sulphuric acid in presence of ether, but could not be crystallised. It develops a purplish-brown coloration on the addition of ferric chloride to an alcoholic solution.

Pelargonidin Chloride 3 : 4'-*Dimethyl Ether.*—Through a solution of the hydroxymethylene derivative (1·2 g.) described in the last section and phloroglucinol (0·73 g.) in ether (20 c.c.), hydrogen chloride was led for 1 hour. The dark crimson crystals (0·6 g.) were crystallised by solution in hot very dilute hydrochloric acid which was brought up to 5% after filtration (Found, in material dried in a vacuum : C, 58·0, 58·0 ; H, 5·0, 5·0. $C_{17}H_{15}O_5Cl,H_2O$ requires C, 57·9 ; H, 4·8%). The reactions of this product were identical with those of a specimen of dimethylpelargonidin chloride obtained from 2 : 4 : 6-triacetoxybenzaldehyde as described by Pratt and Robinson (*loc. cit.*), but the latter was anhydrous. We therefore crystallised the specimen (P. and R.) under the conditions employed above, but nevertheless got the same results as before (Found : C, 60·7 ; H, 4·7. Calc. for $C_{17}H_{15}O_5Cl$: C, 61·0 ; H, 4·5%). The *perchlorates* derived from both specimens were obtained by crystallisation from acetic acid in dark crimson, plank-shaped crystals of identical appearance. The hydrated-chloride specimen melted with decomposition at 221°, and that derived from the anhydrous chloride (P. and R.), and also an intimate mixture of the two, at 220°.

Pelargonidin Chloride.—Dimethylpelargonidin chloride (2 g., prepared as described above), phenol (12 g.), and hydriodic acid (50 c.c. ; d 1·7) were heated together at 150° for 30 minutes. The crystals which separated on cooling were collected, washed with ether, and the iodide was converted to chloride by means of precipit-

ated silver chloride and a little hydrochloric acid in hot methyl-alcoholic solution (35 c.c.). The filtered solution was mixed with 6% hydrochloric acid (50 c.c.), and 0·7 g. crystallised on standing (Found, in material dried in a vacuum : C, 55·9, 56·0; H, 4·2, 4·2, $C_{15}H_{11}O_5Cl,H_2O$ requires C, 55·5; H, 4·0%). This material exhibited the chief reactions of pelargonidin, but was not pure and the crystals did not possess a sufficient resemblance to those of pelargonidin chloride to render identification certain. A small specimen of undoubted pelargonidin chloride was, however, obtained as follows. The crude chloride was converted into iodide by crystallisation from a mixture of hydriodic acid and phenol and, after transformation of the iodide to chloride in the usual manner, 7% aqueous hydrochloric acid was added to the alcoholic solution, and the latter evaporated in a vacuum. The first fraction of nearly square-cut prisms was not quite homogeneous and was recrystallised in the same way. Twinned prisms were obtained and these were thrice recrystallised from very dilute hydrochloric acid solution by the addition of concentrated acid. At first, fern-like masses and then clusters of flat prisms were obtained. Recrystallisation by the evaporation of an alcoholic solution to which 7% hydrochloric acid had been added gave thick prisms which had the characteristic shape of those described by Willstätter and Burdick (*Annalen*, 1916, 412, 163) and of which microphotographs were reproduced. The specimen exhibited the solubility relations, reactions, and absorption spectrum in alcoholic solution of pelargonidin chloride, but this was also true of specimens which nevertheless did not crystallise in the form regarded as typical of the pure anthocyanidin.

CLXV.—*Nitration of the Carbonate and Ethyl Carbonate of m-Hydroxybenzaldehyde.*

By FREDERICK ALFRED MASON.

THE nitration of *m*-hydroxybenzaldehyde has been frequently investigated (Farbwerke vorm. Meister, Lucius, & Brüning, D.R.-PP. 18016, 20116; Tiemann and Ludwig, *Ber.*, 1882, 15, 2044, 2052, 3052; Schnell, *Ber.*, 1884, 17, 1381; Ulrich, *Ber.*, 1885, 18, 2571; Tiemann, *Ber.*, 1889, 22, 2339, 2347; Pschorr

and Seidel, *Ber.*, 1901, **34**, 4000; Friedländer and Schenck, *Ber.*, 1914, **47**, 3040; Henry and Sharp, J., 1924, **125**, 1049), and Friedländer and Schenck have shown that from 100 g. of the aldehyde 40 g., 36 g., and 12 g. of the 6-, 4-, and 2-nitro-derivatives, respectively, are produced.

In view of the orienting effect of the carbonate group, shown, for instance, in the case of *p*-tolyl carbonate, which nitrates almost exclusively in the meta-position to the carbonate group, whilst *p*-cresol itself nitrates chiefly ortho to the hydroxyl group, the nitration of the carbonate and ethyl carbonate of *m*-hydroxybenzaldehyde has been examined in order to ascertain the position of the nitro-group in the products.

In both cases nitration was effected chiefly in position 6, the yield of 6-nitro-3-hydroxybenzaldehyde isolated after hydrolysis being about 83% of the theoretical in the case of the carbonate, the product crystallising in an almost pure condition when the solution of the hydrolysed carbonate was acidified. This process therefore offers an excellent method for the preparation of the 6-nitro-compound, as the older method of direct nitration of *m*-hydroxybenzaldehyde involves a laborious process of separation by fractional crystallisation.

EXPERIMENTAL.

[In part, with H. JENKINSON.]

m-*Aldehydophenyl Carbonate.*—The direct addition of carbonyl chloride to a solution of *m*-hydroxybenzaldehyde in the calculated quantity of aqueous sodium hydroxide gave a mixture of about equal parts of the carbonate and free hydroxybenzaldehyde.

To a solution of *m*-hydroxybenzaldehyde (122 g.) and sodium hydroxide (40 g.) in water (1200 c.c.), saturated sodium carbonate solution (500 c.c.) was added and the whole saturated with sodium chloride, any precipitate formed being ignored. The deep red solution was diluted with crushed ice (500 g.), transferred to two 1½-litre flasks connected in series, and carbonyl chloride was passed in slowly so that about one bubble escaped from the exit tube in 2 seconds. After 1 hour, the two flasks were interchanged and the current of carbonyl chloride was continued for ½ hour; at this stage, the solutions were almost colourless and pasty. The gas was then passed in rather more rapidly and the flasks were shaken; after a few minutes, frothing commenced, due to evolution of carbon dioxide; the gas was passed for a further 20—30 minutes and then stopped. The temperature usually remained well below 40°, the whole operation occupying about 2 hours. The white precipitate

was practically freed from sodium chloride by washing with water, ground up with 100 c.c. of glacial acetic acid, washed with water and with alcohol, dried, and crystallised from glacial acetic acid; m. p. 132—134°, yield about 122 g. (90%). The carbonate is sparingly soluble in most organic solvents and is readily hydrolysed by aqueous alkalis.

Nitration.—The finely powdered carbonate (54 g., free from sodium chloride) was added slowly to 98% sulphuric acid (600 c.c.) at 0° with vigorous stirring and cooling, in a freezing mixture. A mixture of 90% nitric acid (20 c.c.) and concentrated sulphuric acid (100 c.c.) was run in slowly during ½—1 hour, the temperature being kept at 0—5°; after being stirred for ¾ hour, the brownish-black liquid was poured on to crushed ice, when 4-nitro-3-alde-hydophenyl carbonate separated as a pale buff-coloured, granular solid. After 24 hours, the product was collected, washed with water until free from acid, then with alcohol, dried on the water-bath (yield about 70 g.; 97%), and crystallised from glacial acetic acid. The carbonate melts at 194—198° (decomp.), softening somewhat below this temperature (Friedländer and Schenck, *loc. cit.*, p. 3044, give 202°). It is insoluble in hot alcohol, tetra-chloroethane, acetone, or benzene, but is readily soluble in hot glacial acetic acid or nitrobenzene (in the latter case with considerable decomposition). It discolours on exposure to light.*

Hydrolysis of the Nitro-carbonate.—The nitro-carbonate (35 g.) was added in quantities of about 5 g. to 200 c.c. of 4% sodium hydroxide, heated on a water-bath, a small extra amount of alkali being added finally if necessary. The solution was neutralised with acetic acid and cooled in a freezing mixture for a few hours. The dark brown, crystalline product (yield about 31 g.; 95%) was crystallised several times from 10% aqueous alcohol; it then melted at 167°. 6-Nitro-3-hydroxybenzaldehyde is slightly soluble in water or ether, soluble in acetone, glacial acetic acid, nitrobenzene, or pyridine, very soluble in methyl or ethyl alcohol, and insoluble in chloroform, benzene, or toluene. It has very marked sternu-tatory properties, the presence of a few mg. in the atmosphere causing violent sneezing. The identity of the substance was proved by its melting point, by the sensitiveness to light characteristic of *o*-nitrobenzaldehydes, and by its conversion into the yellow methyl ether, m. p. 83—84°, which, on treatment with acetone and dilute alkali, gave the corresponding dimethoxyindigotin.

m-*Aldehydophenyl Ethyl Carbonate.*—To a cooled, filtered solu-

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* On several occasions, under the same experimental conditions, the nitro-product became tarry during filtration, but it still gave a nearly normal yield on hydrolysis.

tion of *m*-hydroxybenzaldehyde (122 g.) and sodium hydroxide (40 g.) in water (900 c.c.), ethyl chlorocarbonate (108·5 g. = 95 c.c.) was added with stirring during ¾ hour, the temperature rising to 30°. The mixture was stirred for ½ hour, and the oily product isolated by means of ether; it distilled almost entirely at 165—167°/20 mm. (yield 184 g.; 95%) as a viscous, colourless or pale yellow oil, *d* 1·42, which was insoluble in water.

The ethyl carbonate is quite stable in an ordinary stoppered bottle. It boils under normal pressure at 289—292° with slight decomposition and does not crystallise, even in a freezing mixture. It is slowly hydrolysed by warm aqueous alkalis, but is more resistant than the carbonate.

Nitration.—The ethyl carbonate (48·6 g. = 34·2 c.c.) was dropped into a mixture of 3% oleum (200 c.c.), 96% sulphuric acid (200 c.c.), and 90% nitric acid (20 c.c.) during 2 hours with good stirring, the temperature being kept below 5°. After 2 hours' stirring, the product was poured on to ice, and the finely crystalline precipitate was well washed with water, pressed, and dried on the water-bath (yield 45·8 g.; 96%).

The product appeared to be a mixture, which has not been separated, but after two crystallisations from benzene–light petroleum (b. p. 60—80°) about half of it was obtained in nearly colourless crystals, m. p. 63—65°. Hence the crude nitration product seems to consist of at least 50% of this (4-nitro) isomeride.

Hydrolysis of 4-Nitro-3-aldehydophenyl Ethyl Carbonate.—The crude nitration product (13 g.) was suspended in water (50 c.c.), the calculated quantity of dilute sodium hydroxide solution added gradually, and the mixture boiled for a short time until the oil had disappeared. The solution was cooled, acidified with glacial acetic acid (7 c.c.), and cooled in ice. The yellow, crystalline precipitate was identified as 6-nitro-3-hydroxybenzaldehyde (yield 3·4 g.; 41%).

Note on some Derivatives of 6-Nitro-3-hydroxybenzaldehyde.

As the simple derivatives are not very fully described in the literature, some experiments were done upon their methods of preparation.

The methyl ether, m. p. 83°, was obtained in 90% yield by stirring methyl sulphate (126 g.) in a solution of 6-nitro-3-hydroxybenzaldehyde (83·5 g.) and sodium hydroxide (30 g.) in water (350 c.c.) at 40°, more alkali being occasionally added until a permanent alkaline reaction was obtained; 6-nitro-3-methoxybenzaldehyde was precipitated in a crystalline condition.

The monoacetyl derivative, m. p. 74° (Friedländer and Schenck

loc. cit.), was obtained by acetylation with acetyl chloride and pyridine; and a *triacetyl* derivative, m. p. 120°, by the action of acetic anhydride and a drop of sulphuric acid at 40—50° and dilution with water.

The benzoyl derivative, m. p. 104—105°, was obtained in quantitative yield by means of pyridine and benzoyl chloride.

The *phenylhydrazone*, m. p. 185—195° (decomp.), separated in red crystals on mixing the aldehyde and phenylhydrazine in acetic acid solution. The sodium salt forms deep red crystals melting above 270°.

The *oxime* forms pale yellow needles, m. p. 179—180°; it is very easily soluble in alcohol and forms an orange-red sodium salt.

The *semicarbazone*, prepared in the usual way, forms pale yellow crystals, decomp. 245—260°. It is soluble in alcohol and forms an orange sodium salt.

CLXVI.—*The Tautomerism of Dyads. Part III. The Effect of the Triple Linking on the Reactivity of Neighbouring Atoms.*

By EDITH HILDA INGOLD.

THE chemistry of substances containing an acetylenic linking has, on the whole, been investigated more from the point of view of the reactions of the unsaturated centre itself, than of its effect on the other atoms in the molecule. Effects of the latter kind are, nevertheless, remarkable, and to direct attention to them is the purpose of this paper.

There is a profound difference between ethylenic and acetylenic bonds, for a hydrogen atom, when attached to an ethylenic carbon, is firmly bound, but when attached to an acetylenic carbon, is easily replaceable by metals, and, at any rate in certain of the simpler cases, possesses tautomeric mobility (E. H. Ingold, J., 1924, 125, 1528). Very probably this phenomenon is not confined to the simpler cases; for whilst potentially mobile acetylene acids of the type $HC\colon\!C\cdot[CH_2]_n\cdot CO_2H$ are comparatively stable, static acids of the type $CO_2H\cdot C\colon\!C\cdot[CH_2]_n\cdot CH_3$ show a strong tendency to acquire an

acetylenic hydrogen * atom by loss of carbon dioxide. This behaviour is analogous to that of blocked triad systems, and suggests that the tendency to form a mobile structure may, in both cases, determine the extrusion of a group. The fact that acetylenedicarboxylic acid, on gentle heating with water, loses only one molecule of carbon dioxide further supports this view, for both carboxyl groups, being similarly situated with reference to the triple bond, should be eliminated if the group ·C:C·CO$_2$H possessed intrinsic instability.

The anomalous effect of the acetylenic linking is particularly marked in the case of the halogen derivatives of acetylene (E. H. Ingold, *loc. cit.*). Thus the normal order of reducibility of halogens in corresponding structures, *viz.*, I>Br>Cl, is inverted in the case of the dihalogenacetylenes, di-iodoacetylene being the most stable, and dichloroacetylene the least.

Again, Feist's failure (see also the experimental portion of this paper) to obtain simple condensation products between ethyl tetrolate and ethyl oxalate (*Annalen*, 1906, **345**, 108) forms a striking contrast with the condensation of ethyl crotonate with ethyl oxalate (Lapworth, J., 1901, **79**, 1276), and appears to show that there is a marked difference in the power of ethylenic and acetylenic linkings to transmit an activating effect from an α- to a γ-carbon atom.

In view of the close connexion between triad tautomerism and γ-activation (Lapworth, *loc. cit.*), it was considered of interest to determine whether the dyad changes associated with the acetylenic linking would have their counterpart in the production of β-activation, that is, whether the influence of a carbethoxyl group can be transmitted through an acetylenic linking to the β-carbon atom. The experiments now described show that this can occur, and that the β-hydrogen atom in propiolic ester is so reactive that it not only undergoes Claisen condensations, with loss of alcohol, with compounds such as ethyl oxalate, but also undergoes the Michael addition reaction with, for example, ethyl fumarate. As the acetylenic hydrogen atom in a hydrocarbon shows a certain amount of reactivity, for instance, towards aldehydes † (Nef, *Annalen*, 1899, **308**, 281; Moureu and collaborators, *Bull. Soc. chim.*, 1902, **27**, 361 *et seq.*), it was thought that the condensations of propiolic esters might be due solely to the grouping HC:C. Experiments showed, however, that amylacetylene does not condense with ethyl oxalate under conditions similar to those used for the corresponding condensations with propiolic esters. It follows that the

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* The term is used in this paper for hydrogen in the combination ·C:CH.

† Formic esters also react in certain cases, and may be included under the term " aldehyde."

carbethoxyl group in propiolic esters definitely enhances the reactivity of the acetylenic hydrogen atom. The phenyl group also appears to enhance the effect of the triple bond to a small extent, for phenylacetylene combines with certain substances which will not unite with amylacetylene (Moureu and Delange, *loc. cit.*, p. 378).

Owing to the tendency of triple-bonded structures to add on sodium ethoxide, the Claisen reactions between methyl and ethyl propiolate on the one hand, and oxalic and benzoic esters on the other, were carried out in the absence of alcohol. The products, however, showed marked instability, and their tendency to pass into other substances during isolation was such that, in the later experiments, the mixture of acids obtained after hydrolysis of the condensation product was completely reduced to the corresponding fully saturated compounds. When, for example, methyl propiolate and methyl oxalate were employed, the principal reduction product was glutaric acid, the formation of which must be represented by the following scheme :

$$CO_2Me \cdot CO_2Me \xrightarrow{CH:C \cdot CO_2Me} CO_2Me \cdot CO \cdot C:C \cdot CO_2Me$$

$$CO_2H \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H \longleftarrow CO_2H \cdot CO \cdot C:C \cdot CO_2H$$
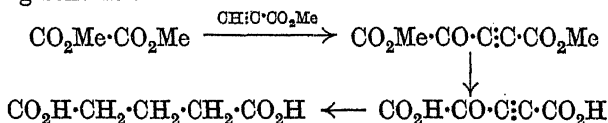
Evidence that methyl oxalate had also combined to some extent with two molecules of methyl propiolate was provided by the isolation of a small quantity of catechol :

$$\begin{matrix} CO_2Me \\ CO_2Me \end{matrix} + \begin{matrix} CH:C \cdot CO_2Me \\ CH:C \cdot CO_2Me \end{matrix} \longrightarrow \begin{matrix} CO \cdot C:C \cdot CO_2Me \\ CO \cdot C:C \cdot CO_2Me \end{matrix}$$

$$\begin{matrix} HO \cdot C:CH \cdot CH \\ HO \cdot C:CH \cdot CH \end{matrix} \longleftarrow \begin{matrix} CO \cdot C:CH \\ CO \cdot C:CH \end{matrix} \longleftarrow \begin{matrix} CO \cdot C:C \cdot CO_2H * \\ CO \cdot C:C \cdot CO_2H \end{matrix}$$
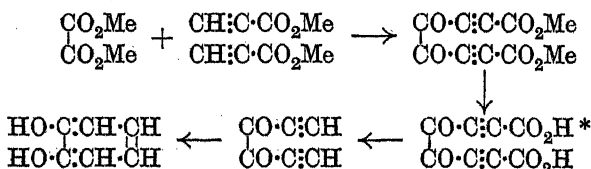
Similar results were obtained in the condensation of ethyl propiolate with ethyl benzoate, the product, after hydrolysis and complete reduction, yielding γ-phenylbutyric acid. If, before hydrolysis, the crude product was distilled, ethyl phenylpropiolate was produced, evidently from the keto-ester by loss of carbon monoxide :

$$C_6H_5 \cdot CO_2Et \xrightarrow{CH:C \cdot CO_2Et} C_6H_5 \cdot CO \cdot C:C \cdot CO_2Et$$

Hydrolysis and reduction | Heat

$$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H \qquad C_6H_5 \cdot C:C \cdot CO_2Et + CO$$
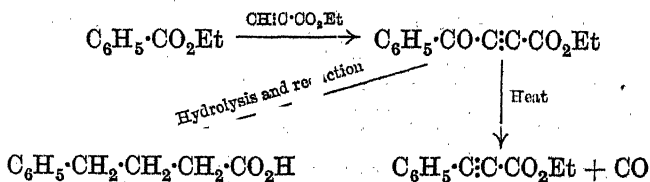
* Examples of loss of carbon dioxide from analogous acetylenic acids are given on p. 1199.

Ethyl propiolate combined readily with ethyl fumarate, and the product, after hydrolysis and reduction, yielded n-butane-$\alpha\beta\delta$ tricarboxylic acid. A portion of the original addition product underwent a redistribution of valency resulting in the loss of carbon dioxide and the formation of muconic acid :

$$
\begin{array}{c}
\text{CH·CO}_2\text{Et} \\
\| \\
\text{CH·CO}_2\text{Et}
\end{array}
+
\begin{array}{c}
\text{H} \\
\| \\
\text{C:C·CO}_2\text{Et}
\end{array}
\longrightarrow
\begin{array}{c}
\text{CH}_2\text{·CO}_2\text{Et} \\
\text{CH·CO}_2\text{Et} \\
\text{C:C·CO}_2\text{Et}
\end{array}
$$

$$
\begin{array}{c}
\text{CH·CO}_2\text{H} \\
\| \\
\text{CH} \\
\text{CH:CH·CO}_2\text{H}
\end{array}
\xleftarrow{-\text{CO}_2}
\begin{array}{c}
\text{CH}_2\text{·CO}_2\text{H} \\
\text{CH·CO}_2\text{H} \\
\text{C:C·CO}_2\text{H}
\end{array}
\qquad
\begin{array}{c}
\text{CH}_2\text{·CO}_2\text{H} \\
\text{CH}_2\text{·CO}_2\text{H} \\
\text{CH}_2\text{·CH}_2\text{·CO}_2\text{H}
\end{array}
$$
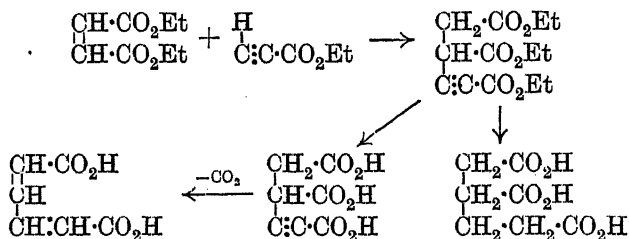
This loss of carbon dioxide during intramolecular rearrangement is reminiscent of Baeyer's experiences with the dihydroterephthalic acids (*Annalen*, 1892, **269**, 170).

Having established the fact that the influence of a carbethoxyl group can be transmitted by an acetylenic linking to the β-carbon atom, it seemed desirable to enquire whether it could not also be carried to the γ-carbon atom. The experiments, however, were inconclusive. Feist's experiments on the condensation of ethyl oxalate with ethyl tetrolate (*loc. cit.*) were repeated, and the reduction method was applied to the products. If the condensation were to proceed in the expected manner, the reduction products should be adipic and sebacic acids (compare the schemes on p. 1201). No trace of either acid could be obtained. Both the possible original condensation products, however, offer, at the methylene groups, points for further attack by the oxalic ester, so that a large number of substances could be formed. On this account, failure to recognise any product does not prove that reactions of the type indicated do not occur.

From the examples given, namely, (1) the dyad migration of hydrogen in acetylenes, (2) the inversion of the usual order of reactivities of chlorine, bromine, and iodine in the halogen acetylenes, (3) β-activation in acetylene esters, it is clear that the effects induced by, or transmitted through, the acetylenic linking are governed by special principles distinct from (and, in some respects, opposite to) those which control the corresponding phenomena in which ethylenic linkings are concerned.

<div style="text-align:center">E X P E R I M E N T A L.</div>

Preparation of Propiolic Acid.—Chlorofumaryl chloride (Perkin, J., 1888, **53**, 695) (100 g.) was dropped very slowly, with continual

shaking, into $3N$-ethyl-alcoholic potassium hydroxide (1300 c.c.) cooled in a freezing mixture. The mixture of potassium chloride and potassium acetylenedicarboxylate obtained (about 210 g.) was dissolved in water (about 450 c.c.), treated with dilute sulphuric acid (60 g. of a mixture of 700 c.c. of water with 300 c.c. of sulphuric acid), and the precipitated potassium hydrogen acetylenedicarb-oxylate (90 g.) heated with water (160 c.c.) for 1 hour on the steam-bath. The filtered solution was acidified with sulphuric acid (62 g. of the above strength), extracted thrice with ether (1 litre each time) dried with sodium sulphate, and distilled under diminished pressure (yield about 100 g. from 680 g. of chlorofumaryl chloride). This process has the advantage over Perkin and Simonsen's (J., 1907, **91**, 843) in that the preparation of dibromosuccinic acid in quantity is avoided.

Methyl Propiolate.—Sulphuric acid (2·85 g.) was added, with cooling, to propiolic acid (9·5 g.) dissolved in pure methyl alcohol (20 c.c.). After being kept for 2 days at the ordinary temperature, the mixture was poured into iced water and extracted with ether. The ethereal solution was washed with sodium hydrogen carbonate solution to remove unchanged propiolic acid (which was recovered), dried with calcium chloride, and distilled through an efficient fractionating column, 6·3 g. of *methyl propiolate* being obtained as a colourless, lachrymatory liquid, b. p. 102°/742 mm. (Found: C, 57·0, H, 5·0. $C_4H_4O_2$ requires C, 57·15; H, 4·8%).

Ethyl propiolate was prepared by Perkin and Simonsen's method (*loc. cit.*). Yield 5·5 g. from 9·5 g. of propiolic acid.

Action of Alcoholic Sodium Ethoxide on Ethyl Propiolate : Formation of Ethyl ββ-Diethoxypropionate.—The ester (4·9 g.), diluted with ether, was added slowly to alcoholic sodium ethoxide (from 1·15 g. of sodium and 15 g. of alcohol), also diluted with ether, and the mixture was poured into water and extracted with ether. The *ethyl ββ-diethoxypropionate* recovered from the ethereal extract boiled at 206°/754 mm. (Found : C, 56·4; H, 9·4. $C_9H_{18}O_4$ requires C, 56·8; H, 9·5%).

Claisen Reactions with Propiolic Esters.

Methyl Propiolate and Methyl Oxalate.—In the preliminary experiments, the products of condensation, which was carried out as described below, were separated into neutral and acid portions in the usual way, with ether and sodium carbonate. Both fractions gave a deep yellow colour with sodium hydroxide, and an intense red colour with ferric chloride; but by hydrolysis only oxalic acid could be obtained, and all attempts to isolate the methyl αγ-diketo-glutarate (from $CO_2Me \cdot CO \cdot C:C \cdot CO_2Me$), probably present in the

neutral fraction, were frustrated by the extensive decomposition which ensued on distillation. The following method of experiment was therefore followed. Methyl propiolate (5 g.) was added to finely-divided sodium (1·37 g.) mixed with a solution of methyl oxalate (7·04 g.) in pure dry ether (110 c.c.). The mixture was heated on the steam-bath for 5 hours, when much darkening took place, and, after keeping over-night, the undissolved sodium was decomposed by the addition of ice. The solution was acidified, extracted with ether, and the extract separated into neutral, acid, and quasi-acid * fractions.

The neutral fraction was heated under diminished pressure on the steam-bath to remove unchanged esters, and the dark brown residue, after hydrolysis with cold methyl-alcoholic potassium hydroxide, was poured into water, and most of the methyl alcohol removed by a stream of air at the ordinary temperature. The product was reduced by Clemmensen's method, amalgamated zinc being added to the strongly acidified solution, which was kept for 1 day at the ordinary temperature, and 1 day on the steam-bath, when it became almost colourless. Ether extracted from the cooled product a mixture of solid acids, which were dissolved in water (100 c.c.), neutralised with ammonia, and treated with calcium chloride, when a precipitate of calcium oxalate was produced. The filtrate was evaporated to small bulk (10 c.c.), and treated with barium chloride, when a very small precipitate of barium succinate was produced. (For the succinic acid, m. p. 184°, obtained from this precipitate, found : M, 117. Calc., M, 118.) After removal of the barium succinate, the filtrate was evaporated, acidified, and extracted with ether, which removed glutaric acid (0·8 g.), identified by m. p. 94°, mixed m. p., and analysis (Found : C, 45·3; H, 5·9. Calc., C, 45·5; H, 6·0%).

A small amount of oxalic acid was separated from the acid fraction, and the oily residue was mixed with the quasi-acid fraction, hydrolysed, reduced by Clemmensen's method, and the products extracted, as above described. After the ether had been evaporated and the dark brown oily product kept in a desiccator, crystals separated, which, on crystallisation from benzene, yielded prisms, m. p. 105°, which were identified as catechol by the colour reaction with ferric chloride, a mixed melting-point determination, and analysis (Found : C, 65·6; H, 5·3. Calc., C, 65·5; H, 5·45%). From the insoluble portion, which contained zinc, oxalic acid was obtained by dissolving in hydrochloric acid, and again extracting with ether.

* This term is used for fractions soluble in sodium hydroxide, but not in sodium carbonate.

Ethyl Propiolate and Ethyl Benzoate.—In the preliminary experiments ethyl benzoate (4·6 g.) was condensed with ethyl propiolate (3 g.), and the products were separated into neutral and acid fractions as described in the previous experiments. The reaction was more vigorous in this case, and a considerable quantity of tar was formed. The neutral fraction was distilled under diminished pressure, when ethyl benzoate (3·6 g.) was recovered. Decomposition then occurred, but a few drops of a high-boiling oil were collected, and identified as ethyl phenylpropiolate by the fact that on hydrolysis (with concentrated aqueous potassium hydroxide) phenylpropiolic acid was obtained, m. p. and mixed m. p. 137° (Found : C, 73·9; H, 4·1. Calc., C, 74·0; H, 4·1%).

The acid fraction yielded a small amount of a brown oil giving a red colour with ferric chloride, and probably containing the diketonic acid (compare p. 1203) $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CO_2H$, but no solid product could be isolated.

In the final experiments, the neutral fraction was distilled at 1 mm. from a bath at 118°, when a considerable amount of unchanged ethyl benzoate passed over. The residue was hydrolysed and reduced as in the experiments with ethyl oxalate, when a liquid acid was isolated, which solidified on seeding with γ-phenylbutyric acid, and was identified as this acid by a melting point (47—48°) and mixed melting point determination.

The acid and quasi-acid fractions were resinous, and yielded only a small amount of benzoic acid on sublimation.

Michael Reactions with Propiolic Esters.

Ethyl Propiolate and Ethyl Fumarate.—These reactions were carried out in ethereal solution in the presence of finely divided sodium as previously described, and, as in the above experiments, much darkening occurred. In the preliminary attempts to effect these reactions, water was added to the condensation product, and the neutral portion isolated with ether. Owing, however, to the extensive decomposition on distillation, it was found impossible to isolate any pure product. In the subsequent experiments, therefore, the undistilled neutral product (from 8·78 g. of ethyl fumarate, 5 g. of ethyl propiolate, and 1·17 g. of " molecular " sodium) was hydrolysed with cold methyl-alcoholic potassium hydroxide, and the acids so obtained were reduced by Clemmensen's method. The solid acids obtained after extraction and vacuum desiccation were rubbed with a little ether. The portion soluble in ether was identified as succinic acid by a melting point and mixed melting-point determination. The insoluble portion, after crystallisation first from ethyl acetate and then from benzene and acetone, melted

at 118—120°, and was identified as butane-αβδ-tricarboxylic acid by a mixed melting-point determination and by analysis (Found : C, 44·0; H, 5·2; M, 191. Calc., C, 44·2; H, 5·25%; M, 190).*

The quasi-acid fraction yielded only a trace of resin, but the acid fraction partly solidified on keeping in a vacuum desiccator. The acid melted at about 300°, but as the small quantity available was contaminated by resinous material in a way that made crystallisation from water impossible, its identification as muconic acid was accomplished by conversion (by means of phosphorus pentachloride and alcohol) to ethyl muconate, which was identified by a melting-point (62—64°) and mixed melting-point determination.

Attempted Condensation of Amylacetylene with Ethyl Oxalate.

The amylacetylene (3·2 g.), prepared from heptaldehyde through the dichloride by Limprecht's method (*Annalen*, 1857, **103**, 84), mixed with ethyl oxalate (4·8 g.) was added to finely divided sodium (0·77 g.) in pure, dry ether. When the sodium had disappeared, the product was worked up in the usual way, but only amylacetylene and oxalic acid could be obtained.

Attempted Condensation of Ethyl Tetrolate and Ethyl Oxalate.

Ethyl tetrolate (5 g.), prepared by Stolz's method (Beilstein, "Organische Chemie," II, p. 480), was added to an ethereal solution of ethyl oxalate (6·5 g.) containing finely divided sodium (1 g.) in suspension. The mixture was boiled until the precipitate first formed (compare Feist, *loc. cit.*) disappeared. Ice was added, the solution acidified and extracted with ether, and the extract separated into neutral, quasi-acid, and acid fractions, all of which were dark brown oils. The neutral and quasi-acid fractions were hydrolysed with cold methyl-alcoholic potassium hydroxide, and then all three fractions were reduced as before. The reduction products, however, were largely resinous, and nothing but oxalic acid could be isolated in a pure condition.

* This acid " clings " to the solvents employed for crystallisation with great tenacity, and must be dried at 100° before satisfactory analyses can be obtained.

Chemistry at Interfaces.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON FEBRUARY 26TH, 1925.

By SIR WILLIAM HARDY, M.A., Sec. R.S.

WHEN your Council invited me to deliver this lecture I was conscious more of the honour than of the responsibility. The sense of the former has not faded, but that of the latter has grown to terrifying dimensions. The fact of the matter is that I cannot hope to inform; the best I can do is to take this unique opportunity for propounding certain conundrums which have been forced on my notice during thirty years' work on interfaces and films.

The material I first worked with was proteins—or proteids as they were then called—and my studies led to a frankly chemical explanation of the properties of this singular group. In a physiological laboratory proteins, the physical basis of life, were still regarded as something outside chemistry and incapable of reactions of the ordinary type.

The protein class which attracted me was the globulins. They are singular in that, whilst themselves insoluble in water, they are dissolved as salts by acids, or alkalis, and, in the absence of acids and alkalis, by neutral salts such as sodium chloride. When dissolved by alkali, that is, when they react as acids, they form systems like soaps. Now the remarkable feature is this—I directed attention to it in the Croonian lecture for 1905—that the two types or states of solution, by acid or alkali, or by neutral salt, are discontinuous in the sense that to pass from one to the other the protein must first be precipitated, and that the protein masses are electrically charged in the first type of solution and are not electrically charged in the second type.

In that lecture I directed attention to the fact that while the electrically uncharged system in its phase relations can be homologated with such a straightforward system as that of water, sodium chloride, and succinonitrile, the electrically charged system, with contact potential differences at internal surfaces, manifests the abnormal viscosity, high degree of inertia to change, and other features characteristic of the colloidal state. The electrical aspect of this state has to my mind been too much neglected of late. I believed then, and I believe now, that colloid chemistry has much to gain from someone who will start from the rich literature of the Lippmann period. He, if anyone, may succeed in rescuing that much-abused word " colloid," and bringing it within the four corners of a satisfactory definition.

I tried myself—indeed I have tried many times—but it needed a better physicist than I am. The fundamental difficulty is easily stated. Take, for example, Dupré's equation for the free energy between two phases A and B

$$T_{AB} = T_A + T_B - 2T'_{AB},$$

the question is whether the final term, which gives the gain of work in forming the interface, can or cannot be divided into two which can be written

$$2T'_{AB} = 2T'_{ab} + f(\sigma),$$

when σ and $-\sigma$ are the densities of the electricity on either side of the interface.

$2T'_{ab}$ then is the work done by simple forces of cohesion, and $f(\sigma)$ the work done in forming the electrical layers. You may object at once that such a question is beside the mark, since all cohesive forces are now recognised as being electrical. I submit, however, that there is a real question. Contact potential implies a certain orderly disposition of the electric polarities and, on the chemical side, a corresponding orderly configuration of atoms and molecules with respect to the interface. Is all the free energy peculiar to the interface gathered in this orderly way, or is there a portion which does not directly contribute to the definite distribution of electricity which constitutes a contact potential difference? This question, to my mind, includes the question of the different valencies—co-valency, ionic valency, etc.

The first obvious step towards answering this question was to measure the potential difference between organic fluids and water and see what relation it had to chemical constitution. I made more than one attempt and obtained always an impossible result— namely, that the contact potential difference was almost independent of chemical constitution. The cause of failure is of interest. The only experimental method which suggested itself to me was to measure the movement of a small drop suspended in water in an electric field of known strength, but it seemed to be impossible to preserve so small an area of interface from contamination amidst such a relatively large mass of water.

Consideration of electrified internal surfaces does, at any rate, lead us directly to what I still cling to as the distinctive feature of colloidal solutions, namely, their inertia whereby a state is not defined simply by the temperature, pressure, and components, so far as they can be recognised, but also by the previous history. The path of approach has to be reckoned with. But although internal electrified surfaces give a high viscosity and a slow rate of change, they are not, I think, the whole story.

The theory of these salt globulins is simple. The insoluble protein is dissolved as a molecular compound with the neutral salt, in the same way that silver chloride is dissolved by sodium chloride. But it is rare to find a component in a solution in water which is so uncharged as to show no movement in an electric field. After much search, I found only one clear case—azomethine dissolved in chloroform—and here the fact is not evidence of the absence of a charge on the molecules of azomethine, because the electric flux necessary for electrophoresis was probably not possible.

Possibly there is no great physical interest at the moment in elucidating the molecular mechanism of contact potential—physicists seem satisfied with a simple electronic theory and chemists with a simple ionic theory—that of Nernst, but there is more to learn. What part do polar groups play ? Where in the molecules oriented at an interface is the contact potential situated ? And, above all, what are the conditions which permit of an electric flux ?

The conditions of discharge of such contact fields are of peculiar interest to the biologist, and of basal importance in the study of that difficult subject the corrosion of metals.

Let me give an example which shows the need the biologist has for an intimate analysis of surface energy in terms of contact potential, of tension, and of orientation. The blood of lobsters and crabs flows, not in capillaries, but in large spaces called sinuses, spaces so large that, if one were freely opened, the animal would quickly bleed to death. These sinuses are torn open not infrequently in the misadventures of their lives. They fight, for example, and a great claw is often torn away in the conflict. Loss of blood on these occasions is reduced to a minimum by that natural first aid which serves us all, namely, the faculty of the blood when disturbed to clot. Clotting in this case must be swift, and it is surprisingly swift—the sinuses are plugged almost at once.

It is to the first stage in this process of clotting that I want to direct your attention. There are in that blood certain cells or blood corpuscles which have been called " explosive " cells, because on the slightest disturbance to the chemical or physical balance of the blood they actually do explode. The upset is due simply to contact of the blood with a " foreign body " which may be sea-water, or may be a glass slide. Using suitable precautions, one can get a drop of blood on to the under side of a cover glass and watch the process. By the time the microscope is adjusted the corpuscles nearest the glass have already exploded, but further down in the drop there are still intact cells and one can watch the progress of the disruption moving away from the glass face. A wave of change must start at the interface between the glass and the blood, and

progress through the latter, involving these sensitive corpuscles in its path. What is it at the interface which starts this wave of change ? It has something to do with what might be called inter-facial reactivity—that reactivity which lowers surface tension and increases the contact potential difference. So much we know because, if paraffin wax be substituted for glass, the change does not occur. I have long wanted to trace the effect of chemical constitution upon the phenomenon and have never yet had time. The change will start from a quartz face, but it must be remem-bered that it is unusually difficult to free a quartz face from a film of natural contamination.

The two impressive features of this phenomenon are (1) that a chemical change of catastrophic character can be started at an interface, and (2) that the change can be propagated apparently indefinitely through one of the phases.

You have all heard of nerves, nerve-fibres, and nervous impulses, which last are waves, partly electrical, which are carried by nerve-fibres. A nerve-fibre consists essentially of a fine rod of protoplasm from 2 to 8μ in diameter, and it is an outgrowth from a nerve-cell, These fine rods may attain a prodigious length—in a large animal like a whale, the rods which connect the cells in the spinal cord with some of the more remote parts of skin or muscle must be many yards in length, and each starts from a small object, the nerve-cell, which is only, say, 100μ in diameter. Now the struc-tural integrity and capacity for growth—note especially the latter —of this tenuous filament depend throughout its length entirely upon its connexion with the nerve-cell of which it is an outgrowth, and the interface from which this control irradiates is without doubt that inside the cell between nucleus and cell body. There can be no question of mere gross manufacture and transference of nutriment—the process would require geological time. There must be some kind of static or dynamic balance just as a row of bricks up-ended on an inclined plane would fall if the support at the end were withdrawn.

So far as my limited knowledge goes, there is nothing in the inorganic world to parallel this dependence of structure, relatively or actually far distant, upon the integrity of a particular interface.

Let us form an interface say by bringing a paraffin, or one of the derived acids or alcohols, in contact with a solid face of glass or steel. There will be adhesion and we can now, from evidence derived from more than one source, be certain that the long molecules will be oriented at the solid face with their long axes at right angles to the interface. Does the effect of the interface end there ? The forces involved are of very short range, less than any dimension

of the molecule. Their range is indeed of the order of the distances which separate the atoms in a molecule. But, if there is a mono-molecular layer of oriented atoms formed at the interface, there will be a secondary interface formed between it and the mass of fluid where a random disposition of the molecules holds, and this will have its effect in orienting a second layer of molecules and so on. In fact, I picture the process going on until it is upset by the heat motions. The study of friction furnishes, I believe, proof that this limit set by the heat motions is not reached until several —one cannot say how many—layers of molecules are involved.

One has, therefore, at the interface a new phase—the interfacial phase, we might call it—which is formed with evolution of heat as Leslie pointed out as far back as 1802, in the formation of which, therefore, degrees of freedom are suppressed, and the phase has a configuration or structure which intrinsically is unstable at the given temperature and pressure, and acquires stability only by the intervention of the forces at the interface. Moreover, the phase is the seat of an electric field of prodigious intensity.

I accept the view that the forces at the actual interface—the adhesional forces of the solid—are, in fact, of exceedingly short range, because all those best qualified to judge are agreed as to this—but in some way they make themselves directly felt right through the interfacial phase so that the capacity for withstanding traction—the friction, in short—is never determined by the chemical nature of the lubricant alone, but by the chemical nature of the solid face as well. If it were merely a matter of setting a number of molecules of a given kind on end, layer on layer, the properties of any plane between the layers would depend merely on the par-ticular kind of molecules bounding it. This never is the case— the physical properties of such a plane depend just as much upon the nature of the solids as upon the nature of the molecules.

Gibbs, it will be remembered, introduced with tremendous effect the conception of an interfacial phase, and what we are particularly concerned with is the depth of this phase. Leslie, more than a hundred years ago, pointed out that the intrinsic pressure—not the quantity p in Gibbs's equations, but the van der Waals pressure —is different in this phase from what it is in the body of the fluid contiguous to it.

The first evidence I will bring forward to support the statement that the interfacial phase may be many molecules in depth is final and convincing. Bragg and his fellow-workers have been analysing with the aid of X-rays the structure of thin layers of grease spread upon a solid face, and they find that the long paraffin molecules are oriented end-on to the interface, and that they are disposed in

rows one above another. There is, in fact, as I claimed many years ago, a kind of crystallisation at an interface with the crystal planes disposed tangentially.

There is one observation made by Bragg and his fellow-workers of peculiar interest to me. It will lead to a digression, but I hope an interesting one. They find that the grease when simply placed on the solid does not show this architecture, but develops it rapidly when rubbed or smeared upon the surface. This is, perhaps, what might be expected; the study of friction shows that orientation comes to its maximum slowly even when mobile fluids such as octyl alcohol, or caprylic acid, are used. With the latter, for example, friction falls, owing to gradually increasing orientation at the inter-face, for about 60 minutes at ordinary room temperature (11°). Such a period might be expected to be indefinitely long in a highly viscous grease.

It is really surprising how much mechanical agitation will shorten the period even when the lubricant has high fluidity. With caprylic acid on glass, orientation reaches a maximum, and friction reaches a steady value, when there is no mechanical disturbance, other than earth tremors, in about 60 minutes; but if the surface be disturbed by vigorously moving the slider about, it is completed in about 10 minutes.

It looks as though the first effect of the attraction field of the solid was to lock the molecules in the random disposition charac-teristic of the body of the fluid. Put in another way, the effect of the attraction field is to increase the viscosity of the fluid in the neighbourhood of the solid so that rearrangement under the influence of their polar or other attractions is delayed. There is direct evidence of such a change.

Mechanical agitation materially quickens the process of orient-ation even when the surfaces are covered only by an insensible film deposited from vapour. Consider this case for a moment. Caprylic acid consists of a carbon chain loaded at one end by the carboxyl group. The molecules might therefore roughly be likened to long rods the attraction of which for the solid face is greater at one end than at the other. These rods are, at any instant, disposed at random in the vapour, and therefore, when they move to the solid face, although an excess will strike with the more attracted end, say the carboxyl end, many will strike with the other end. The film as first formed will be far from completely oriented and there is a latent period or lag during which orientation becomes more orderly owing to the evaporation and condensation of molecules into and out of the vapour.

Left to itself, the film reaches a steady state, that is to say,

friction ceases to diminish, in about 10 minutes, but mechanical agitation, produced by motion of the slider about the plate, causes the steady state to be reached in a matter of seconds. Obviously in the second case something more than evaporation and condensation is at work—the molecules in the film must actually rearrange themselves on the spot, and the process of changing ends is hastened by mechanical agitation.

I could multiply instances, especially of the varying degree of sensitiveness to mechanical disturbance. I will take an extreme case, and the case reveals a paradox.

It is possible to deposit films in succession upon a solid face, and friction values reveal that they actually are in succession. The stability of the arrangement obviously depends upon the order in which the films lie. For example, a clean surface of glass or steel can be covered with an insensible film of solid paraffin, or oleic acid, or undecyl alcohol, or undecoic acid, etc., and a second film of water deposited on this film by admitting water vapour. With great care to avoid mechanical agitation, the friction of the doubled film can be observed, but the disposition is highly unstable if the first deposited film is fluid, and almost any degree of movement upsets it with consequent change of friction. Here are the figures for undecyl alcohol :

Alcohol alone.	Water vapour admitted.	Mechanical agitation at once rose to
$\mu = 0.44$	$\mu = 0.33$	$\mu = 0.48$

I see in this an interesting possibility. Let us suppose there is a righting mechanism which, by expenditure of energy, would, given the opportunity, restore the original disposition of the films. I am, of course, thinking of living matter. Such layered films might reach any degree of sensitiveness to mechanical shock, and you obviously have here the germ of the mechanism of a sense-organ capable of reacting to any kind of mechanical disturbance. More than that, by having a succession of films rightly arranged one could get an effect magnified, and it is at any rate noteworthy that in what are believed to be organs of the pressure sense—of traction at any rate—one does get a succession of surfaces about a nerve-ending, like the coat of an onion.

Here we see the importance of not losing sight of the contact difference of potential. These films, no matter how thin, are at a different potential from that of the substance on which they lie. I was able to observe this as far back as 1911; and the fact is, of course, the basis of frictional electricity as Helmholtz recognised, although he did not specify or, I think, visualise an actual film of foreign matter. Any disturbance of the films, whether single or

doubled, is certain, therefore, to produce a redistribution of electricity; so the way for an effect on the end of a nerve fibre is clear.

To complete the story—the possibility of producing a succession of films depends upon the immiscibility of the first-used substance with water. When the substance is miscible with water, unstable states are not produced and water vapour always and at once increases friction.

Benzene vapour, on the contrary, when used in the same way always lowers friction.

Let me pick up the paradox before I forget it. Water is, it will have been noticed, a lubricant in these cases. This is obvious when a plate of solid paraffin is used. Here is a table of values of great interest :

Glass lubricated with tetracosane : $\mu = 0\cdot325$.
Water film formed on the composite surface : $\mu = 0\cdot110$.
Tetracosane on tetracosane : $\mu = 0\cdot060$.
Water film deposited on solid tetracosane from vapour : $\mu = 0\cdot025$.

But water is entirely without lubricating action on clean glass, steel, bronze, quartz, or bismuth. I do not want to be mistaken here. Water, of course, can act as a lubricant in the hydrodynamical sense investigated by Osborne Reynolds. That is to say, if the solids are kept apart by a pad of water held in place by external forces, it has the lubricating properties of a fluid with its physical characters. But in the boundary region, a film of water, or a pool of water, has no power of lowering the friction between these various solids. Yet it can alter the state of the surface of a substance so, in a sense, inimical to itself as a normal paraffin, and reduce the friction by more than 40 per cent. This peculiar feature of water, the limitation of its powers as a lubricant, is at present wholly without explanation.

Water in a sense is an abrasive. It decreases to a startling extent the lubricating powers of all substances with which it is miscible in the boundary zone. A trace of water will destroy the lubricating power of one of the lower alcohols. In this sense, water is a true abrasive, although it has no influence one way or the other on the friction of clean faces.

Glycerol is another of these neutral substances, although owing to its high viscosity it is not easy to get rid of the flotation action. However, if surfaces are forced together through the pad of glycerol, disaster quickly follows. A case was brought to me a few days since of ball bearings, lubricated only with glycerol, in which the balls were quickly torn into fragments. A chemist would, I believe, expect glycerol to behave like water in most respects.

A short while back I postulated a righting moment which should restore a film which had been destroyed. Here is an example

which is remarkable, because the righting moment is exerted at a distance and depends for its operation upon the integrity of another interface.

Eggs of certain starfish, because they are large, have been much studied by the methods of microdissection. A thin film can be detected under the microscope covering the surface of one of these eggs. When this film is pierced and the contents of the egg, the living substance, are injured over a limited area, repair is effected by the re-formation of this surface membrane between the injured and uninjured parts. This is the process of healing. The injured parts are beyond repair and they are simply cut off by this membrane formation. There is here that righting power which I postulated.

But the righting power depends, as in the example given earlier, upon the intactness of the interface between nucleus and cell-body, for if the fine needle is simply pushed into the cell until it punctures the nucleus of the egg, the superficial film, instead of being reformed, perishes over the whole body of the cell and in a curious fashion, for it disappears first about the point of entry of the needle, and then the solution or disappearance progresses slowly over the whole surface. Following on this, the whole cell becomes invaded by water and breaks up.

One must suppose that the influence of the nucleus or the nuclear interface must diminish with distance—the righting power will diminish—and this I cannot but suppose is one of the factors which sets a limit to the size of the living cell.

I will now return from this somewhat long digression to the question of the depth of an interfacial phase and consider it in the light of measurements of friction.

It will be necessary first briefly to summarise the evidence. Consider a flat plate covered with fluid and a heavy body falling under its own weight through the fluid. As it falls it must displace the fluid lying between its lower surface and the plate. The time occupied in falling will, therefore, be a function of the viscosity of the fluid, the area of the plate, the distance through which it falls and, to a remarkable extent, the shape of the surface of the falling body. The equations for the time occupied in falling, which have been worked out by Professor G. I. Taylor, show that whilst the time needed to fall completely through the fluid to the plate is always infinite, the infinity is of a low order if the under surface of the falling body is curved, and of a high order if it is plane.

Calculated with the help of these equations, the time needed to fall through water to a molecular distance from the plate is a matter of hours for a plane slider—as I will call the falling body—and of seconds for a curved slider.

As the layer of lubricant between the faces is thinned by the fall of the slider, one may expect the friction to increase; therefore, by following the changes in friction after the slider has been put in a pool of lubricant, one can follow its fall. There is, in short, a lag or latent period following the placing of the slider in the pool whilst the former is falling through the fluid.

Now when the slider is plane this lag actually lasts for an hour or more, but when it is spherical it is so short as to be indetectable. It must be remembered, however, that it takes 20 seconds to make a measurement of friction.

Before giving actual figures, I must, to avoid misunderstanding, point out that a lag or latent period before a steady state is reached can be due to one or both of two things—to the time occupied in falling through the lubricant, or to the time occupied in the orientation of the molecules of the lubricant with respect to the normal to the surface of the plate. Time does not permit me to give the evidence in detail. It must suffice to say that when paraffins or their derived acids or alcohols are used, lag due to orientation is exhibited only by the latter two classes, in which the two ends of the elongated molecules differ. No lag due to orientation has been detected with certainty when the lubricant is a normal paraffin.

There is another way to discriminate between the two causes. When the lag is due to orientation, friction diminishes during the latent period, but when it is due to thinning of the layer of lubricant friction increases during the latent period.

Here is an example of a latent period of increasing friction due to fall of the slider through the lubricant.

Undecane.

	Pull in grams.	μ.		Pull in grams.	μ.
1 sec.	3·06	0·15 (approx.)	30 mins.	10·98	0·538
5 secs.	6·53	0·32 (,,)	45 ,,	11·14	0·546
1 min.	8·77	0·43 (,,)	60 ,,	11·14	0·546
5 mins.	9·85	0·483	90 ,,	11·20	0·549
10 ,,	10·57	0·517	120 ,,	11·20	0·549
15 ,,	10·83	0·531	180 ,,	11·20	0·549

What is the steady state? Is it a state in which the layer of lubricant has reached a constant value? In other words, has the slider ceased to fall because a layer of definite thickness and of great mechanical stability has been reached? Apparently not, because if additional weight is placed on the slider there is a further rise in friction and another latent period of rising friction which ushers in a new steady state. Similarly, if the weight is reduced there is a latent period of falling friction. In short, the slider

appears to move up or down the fluid according as the load is decreased or increased.

Plane slider of steel, lubricated with a large excess of liquid nonadecane. Latent period measured for increase in weight of slider.

Initial load (g.).	Original μ. (Steady value.)	Weight added (g.).	μ After adding weight. (Steady value.)	Latent period (mins.).
120·4	0·2523	50	0·2441	12
420·4	0·2105	50	0·2055	5
821·2	0·1871	50	0·1857	±1

This process, however, has a limit, for when the load is high enough variations of load are not followed by a latent period.

These various features are best exhibited by a curve (Fig. 1) in which the coefficient of friction, μ = friction/load, is plotted against the pressure between the bearing faces or load/area.

Fig. 1.
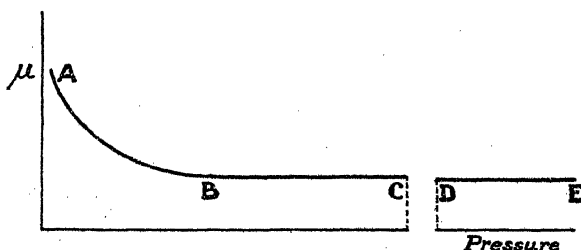
You will notice over the first part of the curve μ is falling. Now this is itself remarkable, for μ is a measure of the efficiency of a lubricant with respect to a single variable, the load. Over this part, AB, there is the latent period characteristic of variations in the depth of the layer of lubricant owing to the slider rising or falling in the fluid. We have, therefore, the curious fact that the efficiency of a lubricant increases as the layer thins until it reaches a maximum at B.

At B over the horizontal part, there is no latent period of the kind mentioned. If any point in BCDE is taken and the load varied, but not enough to trespass on the region AB, the adjustment of the load to the friction is sensibly instantaneous.

There is a fundamental and surprising law of friction, which was formulated by Amontons in 1699, according to which the friction is equal to the load multiplied by a parameter which of course then is the coefficient of friction, μ. This law holds rigidly over BCDE and does not hold over AB.

The part DE refers to a spherical slider. It is obvious that

from its shape the pressure under a spherical slider must be immense, and to indicate this I have broken the scale of pressure. A spherical slider owing to its shape at once cuts right through the lubricant until the limiting layer characteristic of the whole region BCDE is reached, and this alone would explain the fact that one never gets any indication of rising or falling of a spherical slider in the lubricant.

It is not my business here to discuss this curve in detail, that will be done elsewhere. It will suffice if I say that over the region AB the layer of lubricant would appear to be many molecules thick, and that there the adjustment of friction to the load is effected by an actual flowing in and out of lubricant from between the surfaces of slider and plate, whilst over the region BCDE this process ceases and the adjustment of friction to variation in the load is by the elastic forces between the atoms, and for this reason it occurs with a rapidity too great to be detected. It is only when interatomic forces alone are concerned that Amontons's law holds.

I can now take up the question of spreading of effect from the interface.

At A the layer of lubricant is several molecules in thickness, yet the state is far removed from that of the interior of the fluid. The layer can exhibit static friction, that is to say, it can carry a stress without continuous deformation. Somehow, throughout its entire depth, the molecules are to this extent locked in place by the attraction fields of the solids. It is structured throughout and the maintenance of the structure is due to the fields of the solid.

It is legitimate to assume that the plane of slip is midway between the solid faces. If the state of the lubricant were unchanged there, the friction would be independent of the nature of the solid and be a function only of the constant which defined the state of the fluid. This is not so—the same lubricant at the point A in the curve gives entirely different values of friction for different solids. The following table illustrates this :

Steel slider. Face plane. Load 20·4 g., corresponding to point A on Pressure/μ curve. Lubricant octyl alcohol.

Plate.	μ.
Medium carbon steel	0·463
Mild carbon steel	0·457
Nickel chrome steel	0·469
Phosphor-bronze	0·510
Bismuth	0·438
Glass	0·523
Quartz	0·472

I do not want to press this evidence too far, because the experimental conditions were not rigidly controlled, but, under conditions

in which there would appear to have been a layer of water several molecules in thickness between the faces, we find water :

antilubricant for glass on wood
lubricant   ,,   ,,   ,, ebonite
neutral   ,,   ,,   ,, sulphur
               ,,   ,,   ,, glass
               ,,   ,,   ,, steel
               ,, steel ,, steel.

The physical properties of water, which depend upon its molecular structure, are changed by the force-field of the solid and the change penetrates some distance into the fluid.

Further experiments—measurements in the region AB with different solids—will, I hope, enable us to formulate what might be called the law of transmission, that is, the variation in the effect of the field of the solid with distance along the normal. That has been done only in the region DE and to the results I will now turn.

In the region DE the increased pressure has reduced the layer of lubricant to a layer of limiting thickness and of great mechanical stability. I am going to assume that this layer consists of two monomolecular layers, one for each face, that the long molecules in each of these layers are placed on end on the surfaces, and that the plane of slip lies between the two layers midway, that is, between the solid faces. This is pure assumption, justified perhaps by the analogy of certain films on the surface of water, and by the fact that it alone makes it possible to visualise the relations I am about to describe.

Many solids and many lubricants have been investigated in the region DE. I will confine my observations to normal paraffins and their related acids and alcohols. When the coefficient of friction is plotted in relation to molecular weight, we get the curves shown in the diagram (Fig. 2). The curves are straight lines.

I may note, in passing, that in the region AB (Fig. 1) the curves are not straight lines, but concave with the convexity turned to the horizontal axis. There is in fact an infinite number, a family of curves, each corresponding to a particular load and the straight-line curves are merely the limit of this family. We know almost nothing at present of this family.

Going back to the straight-line curves. When a change is made from one solid to another, say from a steel to glass, or one steel to another, the effect is merely to shift all the curves parallel to themselves.

Fig. 2.
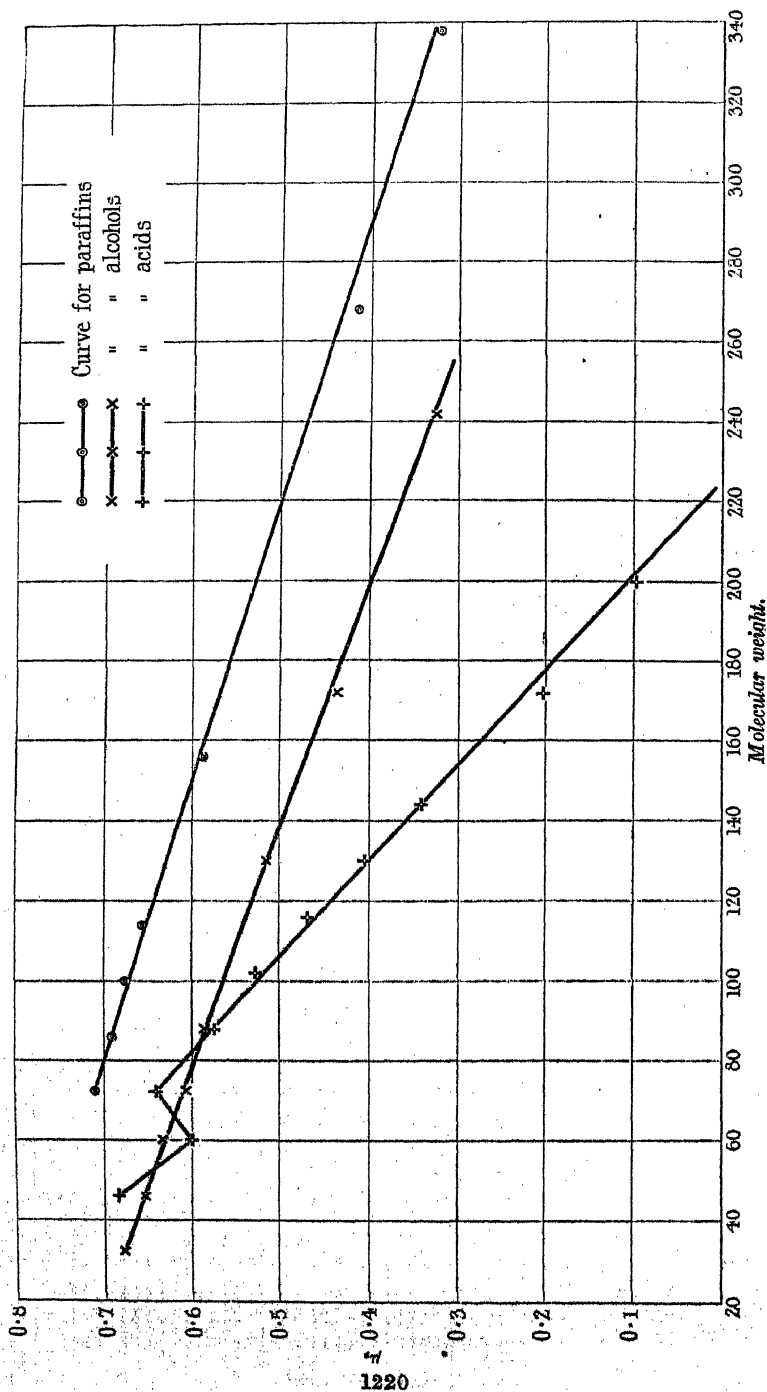
The equation for the curves therefore is

$$\mu = b - aM,$$

where b is a parameter depending upon the chemical nature of the solids and a only upon the chemical series, paraffin, acid or alcohol, as the case may be.

Fig. 2.
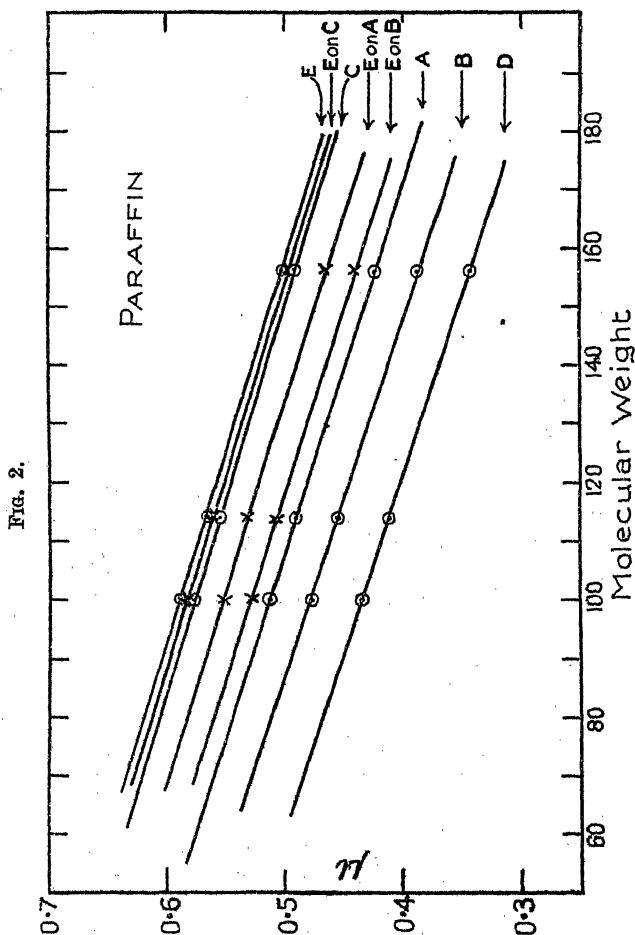
If two different solids are used, if the slider, for example, is of bronze and the plate of steel, each solid produces its effect independently of the other, so that the equation becomes

$$\mu = \tfrac{1}{2}(b_1 + b_2) - aM,$$

where 1 and 2 refer to the two solids.

Now, when the curves for a number of solids were compared a relation was disclosed which was satisfied by the equation

$$\mu = b_0 - d - aM,$$

in which b_0 depends only upon the solid, d only on the chemical series, and a is as before.

Consider now the structure of these molecules. They consist always of end groups CH_3, $CO \cdot OH$, or $CH_2 \cdot OH$, with a carbon chain between. Eliminating aM, which obviously refers to the carbon chain, the parameter d can refer only to the end groups, so we may write as the final form

$$\mu = b_0 - d - c(N - 2),$$

where N is the number of carbon atoms.

This equation is startling in many respects. The parameter b_0 is merely the value of friction when no lubricant is present.

Let us assume that this value is some function of the attraction field at the surface of the solid—indeed this is the only assumption open to us—then the equation means that each atom of the lubricant is responsible for a decrement in this field which is a pure function of its nature and of the configuration. Each atom is, as it were, capable of saturating or neutralising a fixed fraction of the field.

I want you to notice one thing which will mean more to you as chemists than it does to me. The parameter c is the decrement due to each carbon atom. It is a quantity completely independent of the nature of the solid, being the same for solids so different as glass, steel, and bismuth. It is not, however, a fixed property of the carbon in the paraffin chain, but is determined by the nature of the end group. The curves slope differently for acids, alcohols and paraffins.

Obviously, if the chain is long enough, if N is large enough, the field will vanish and there will be no friction. This we have actually observed to this extent, that the smallest traction we could apply produced slip.

Let this happen—let N be large enough to reduce friction to zero—what happens to the field of attraction of the molecules itself? That is the remarkable feature of the equation, the purely negative part played by the molecule of the lubricant.

I raised the question quite early in this lecture, whether all the work done by the cohesive forces other than that dissipated as heat was expended in setting up the contact potential difference. Here is an indication, no more, that it is not.

Friction when the limiting layer alone is involved is, as we have just seen, a linear function of the molecular weight; but the capacity

for reducing the contact potential between water and mercury emphatically is not, as Guyot's measurements show. Like the total work of adhesion to mercury, the capacity for reducing the contact potential increases as the carbon chain lengthens, but not in pro- portion to the lengthening.

We may suppose that b_0, the friction of clean unlubricated faces, is some function of the cohesion field on the face of the solid, and the equation given above then tells us that this field is gradually extinguished as the carbon chains lengthen.

The cohesion between these paraffin substances and the solid faces should therefore increase as the chain lengthens. The cohesion—that is, the work of forming an interface—between these substances and water has been measured and found to depend almost wholly upon the end groups. It is independent of the length of the chain in the alcohols and acids and increases only slightly in the case of the paraffins (e.g., C_6, 19·99; C_{10}, 24·12 dynes per sq. cm.).

But, according to Harkins, with the metal mercury the work of cohesion at the interface increases greatly with the length of the chain (e.g., paraffins, $\pm$ 5 dynes per carbon; alcohols, $\pm$ 10 dynes per carbon).

There is a simple way of showing the effect of a lubricating film upon cohesion. A plate of glass is cleaned, lubricated with a film of insensible thickness, and roughly cleaned as to one-half by passing the flame of a Bunsen burner quickly across it. Clean mercury is now finely sprayed on to the surface, and the plate is then turned upside down; the drops of mercury fall off the lubricated part and remain cohering to the clean part.

Something may be gleaned from the properties of free films as to the distance through which the state at any interface may extend.

It was, I believe, Gibbs who first suggested that a soap film con- sisted of two walls or skins with fluid between. In Reinold and Rucker's papers each wall is taken to be merely the superficial parts wherein surface effects are resident—the depth of each "wall," therefore, was equal to the "range" of the cohesive force.

It is, however, quite easy to construct a film in which the surface wall is without doubt a chemically distinct structure. If a film of, say, oleic acid be formed upon clean water, the density of the film being less than that required to produce the full fall of tension, and a ring of, say, copper wire—that is what I used in my ex- periments—be gently withdrawn from the body of the water, a film is formed over the ring which is of astonishing stability if the

right concentration of the oleic acid on the surface has been hit off. I have passed such a film in lecture round a big class without its breaking.

There can be no doubt here as to the structure of the film. The composite surface has merely been folded together so that there are two skins of oleic acid, AA' in the diagram (Fig. 3); one on each surface with a plate, B, of water between them. By observing the motion of particles under the microscope when a weak electric field is established in the film, it is possible to convince oneself that the skins AA' are at a different potential from the water between them. The skins of oleic acid are always negative to the water.

Many years ago—in 1885—Reinold and Rücker described how the passage of a small current through a soap film would prevent it thinning under the action of gravity. The difference of potential between surface skins and middle plate noted above accounts for this. When one watches such a process under the microscope one sees that the superficial skins show no movement at all, they seem quite rigid, but the internal plate of fluid flows under the influence of the electric field.

Now, if the internal plate of fluid were merely fluid as in mass and unaffected by the interfaces on either side of it, the tension of the film and its specific electric conductivity would be independent of the thickness. This, indeed, is true of a soap film until it thins to about 50 $\mu\mu$, when, as you all know, tension becomes a rapidly varying function of the thickness. If x is the thickness, the sign of the quantity dT/dx changes from negative to positive, and remains so until the thickness falls to that of the black film, which is about 11 $\mu\mu$.

Reinold and Rücker, following a suggestion made by Clerk Maxwell, attributed this change to instability—because the film obviously is unstable when the coefficient is positive—to a change in the force of cohesion from an attraction to a repulsion. They supposed that the force was a repulsion from 50 to 11 $\mu\mu$ and then again became an attraction.

No one I suppose holds that view now. The accepted theory of the stability of free films is based upon the variation of superficial tension of water on whose surface is spread some " active " substance, that is, some substance which lowers the tension. If a free film thins under its own weight for example, the concentration of active substance on its surface diminishes and the tension rises. So long as this happens, the film is stable.

This theory, however, fails to account for the curious instability over certain variations of the total thickness, because in my opinion it concentrates attention on the surface films to the neglect of the

middle plate : yet the microscope shows that it is in the middle plate where adjustment is made to imposed stress.

McBain and Jordan Lloyd, using the ultra-microscope, have shown that the colloidal particles in a solution of soap or gelatin become attached to one another to form threads. In certain solutions of protein, the growth of such threads can be followed with the ordinary microscope, and they are seen to become attached to one another so as to form a framework or sponge.

In a stretched structure such as a soap film the direction of such threads with respect to the tangent will be determined by the lines of stress. I was able to observe this in protein solutions. Let them be disposed in the middle layer, B (Fig. 3), at right angles to the surface with their ends anchored in the interfaces aa, $a'a'$. When the middle layer thins so that the threads can stretch completely across from aa to $a'a'$, a critical point in the history of the film will be reached, for it is known that such threads tend to shorten—

FIG. 3.
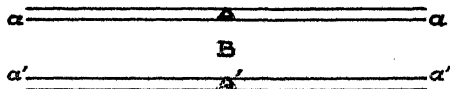
the property of shrinkage, or "synaeresis" as Graham called it, of jellies depends upon this property—and drainage of free fluid from the film will be hastened. If this occurred more rapidly at any point than elsewhere, the tension at that point would fall, and rupture would occur were it not for the stiffening due to the framework.

A soap film is symmetrical in the sense that the films A, A' on each face are the same. When they are not similar, other phenomena appear.

It is easy to make an unsymmetrical film by liberating a bubble of air under water which is covered by a skin of some substance such as oleic acid which is immiscible with it. If the water be chemically pure and freed as far as possible from active substances by scraping its surface, the amount of contamination available for forming a skin on the inner face of the bubble will be very small, and the time available for condensation at the face very short, namely, the time occupied by the bubble in rising through a centimetre or so of water. The density of the skin on the upper surface of the water is under the control of the experimenter and may be varied as desired.

When the bubble has risen to float on the surface, the free film therefore has an exceeding small amount of matter condensed on

its lower surface and can have any density of a known component the operator may desire on its upper surface.

The mechanical stability can be gauged from the time the bubble lasts on the surface. During this period the film will be thinning by drainage of the water in the middle plate, B, and the apex obviously will thin most rapidly. The bubble bursts when, owing to the thinning, the tension begins to fall at the apex.

Now one finds that the duration of the bubbles, that is, the amount of drainage they can stand before they become unstable and burst, is a remarkable function of the tension of the composite surface oleic acid–water, that is, of the density of the acid on the water face.

FIG. 4.
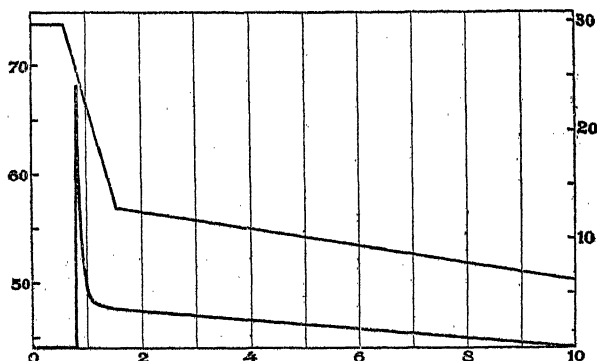
The scale of tension of the general surface of the water is given on the left, and the upper curve is the curve of tension. The time scale in seconds is given on the right, and the lower curve gives the duration of the bubbles. The abscissæ give the calculated thickness of the layer of oleic acid on the surface of the water in $\mu\mu$.

Here is the curve, with the curve of tension also (Fig. 4). You will notice that there are two points at which the bubbles have no stability, that is to say, when they burst at once and with a peculiar, sharp click. The first is the region in which the tension is that of pure water, and the second is that in which the surface of the water is saturated or rather oversaturated with oleic acid. (Other substances give the same result.) But the most striking thing is that one passes from extreme instability to maximum stability at once. There is, in fact, a discontinuity of state.

Why should stability decline as tension falls ? The variation of tension with the concentration of oleic acid cannot be the cause, because the curve relating them appears to be a straight line. In other words, $dT/dF = $ constant.

I suggest that the mechanical stability of the film falls as it becomes less symmetrical owing to the increasing difference

in the density of A and A' (Fig. 3). The amount of contamination on the inner face (A') must be exceedingly small and therefore the two surfaces of the film are most nearly alike in state when the contamination, say oleic acid, on the upper surface, A, is also small in amount.

The water in B is, in short, modified throughout by the interfaces aa, $a'a'$, and when those interfaces are not similar it is like an unannealed plate.

Another instance of the influence of the forces at an interface extending through a layer of fluid many molecules thick is found in the way liquid will cause a ball to stick in a cylindrical hole when it has a clearance of 0·0001 inch. This case is discussed by A. A. Griffith (Phil. Trans., 1920, A, 221, 196), who supposes that the ball is bound to the inner surface of the cylinder by chains of molecules stretching from interface to interface.

A last word as to why a biologist, in spite of the handicap of his imperfect training for the task, is justified in sticking so obstinately to this problem of the distance to which the matter on either side is modified by the field of force at the interface. It is because it offers a slight and precarious but definite foothold in the most obscure region of biology. Growth, and its fellow repair, considered as physical processes are almost wholly beyond existing knowledge. The fidelity with which structure repeats itself is obvious in heredity.

Recent work, if anything, deepens the mystery of living matter, of how it preserves its space pattern, how it can be the *milieu* of chemical processes of peculiar and special kind, how it can maintain within itself sinks and sources of energy. It contains it is true a multitude of suspended particles, but these seem to be merely enclosures. When they are driven to one side, as they can be by centrifuging, the material is an optical vacuum. Take the nucleus —what is it?—apparently no more than a pellicle or skin, a mere bladder containing fluid !

CLXVII.—*The Ionisation of Aromatic Nitro-compounds in Liquid Ammonia. Part I.*

By (Miss) MARGARET JOYCE FIELD, WILLIAM EDWARD GARNER, and CHRISTOPHER CAIGER SMITH.

ORGANIC nitrogen compounds undergoing ionisation in liquid ammonia may be classified into three main groups : (1) amides and imides the conductivity of which arises from their behaviour as " ammono-acids," (2) aliphatic nitro-compounds which conduct

through the production of ammonium salts of pseudo-acids, and (3) aromatic nitro-compounds the mode of ionisation of which is yet uncertain. Of the last class, Kraus and Franklin (*Amer. Chem. J.*, 1900, **23**, 277; *J. Amer. Chem. Soc.*, 1905, **27**, 197; *Z. physikal. Chem.*, 1909, **69**, 272) have studied a number of mono-, di-, and tri-nitro-derivatives and the results they obtained with *o*-, *m*-, and *p*-dinitrobenzene have indicated that the conductivities in liquid ammonia are very sensitive to changes in the position of the nitro-group in the benzene ring. Thus the conductivities of solutions of *m*-dinitrobenzene were comparable in magnitude with those of typical salts in ammonia, whereas *o*- and *p*-dinitrobenzenes were comparatively feebly ionised in solution.

These authors have not, however, considered the mechanism of the ionisation of this class of nitro-compounds.

If the ionisation of aromatic nitro-compounds, as in the corresponding aliphatic substances, occurs through the formation of an ammonium salt of a pseudo-acid, then, on electrolysis of a solution in liquid ammonia, organic ions would be discharged at the anode and ammonium ions at the cathode with the liberation of hydrogen gas. The direction of movement of the organic ions of *m*-dinitrobenzene in an electrical field is in agreement with this view, but since electrolysis is not accompanied by the liberation of hydrogen at the cathode and as the hydrogen is not used up to any marked extent in reducing the nitro-compound, it can be definitely stated that the ionisation does not occur through the formation of the ammonium salt of a pseudo-acid. Also, since the cathode solution after the electrolysis is colourless, consisting solely of anhydrous ammonia with a high resistance, it appears that the ionisation of *m*-dinitro-derivatives is of an unusual type.

The kation is very probably an ammonia molecule carrying one or possibly two positive charges. The ionisation may thus be analogous to that discovered by Kraus for solutions of sodium in liquid ammonia, which occurs according to the equation $Na + xNH_3 \longrightarrow Na^+ + xNH_3^-$, a negatively-charged ammonia ion being produced. It is suggested that in the case of the *m*-dinitro-derivatives the ionisation occurs according to an equation of the type

$$(1)\ R(NO_2)_2 + xNH_3 \rightleftharpoons R(NO_2)_2,xNH_3 \rightleftharpoons R(NO_2^{--})_2 + xNH_3^+,$$
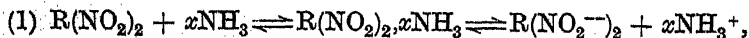
the values of x and the magnitude of the charges on the anion and kation being for the present unknown. On electrolysis, the colourless ammonia ion travels to the cathode, is discharged, and becomes an ordinary solvent molecule.

In many respects, the above two types of ionisation are analogous to those occurring in cataphoresis experiments with colloids, and

it is not impossible that the anion of the nitro-compound may be a colloidal particle with high mobility. In any case, its constitution is of considerable interest. The following is suggested as a possible mechanism for the ionisation

$$R-N\diagdown_{O}^{O} + 2e = R-N\diagdown_{\overline{O}}^{\overline{O}},$$
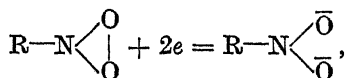
the nitro-group acquiring two negative charges.

FIG. 1.
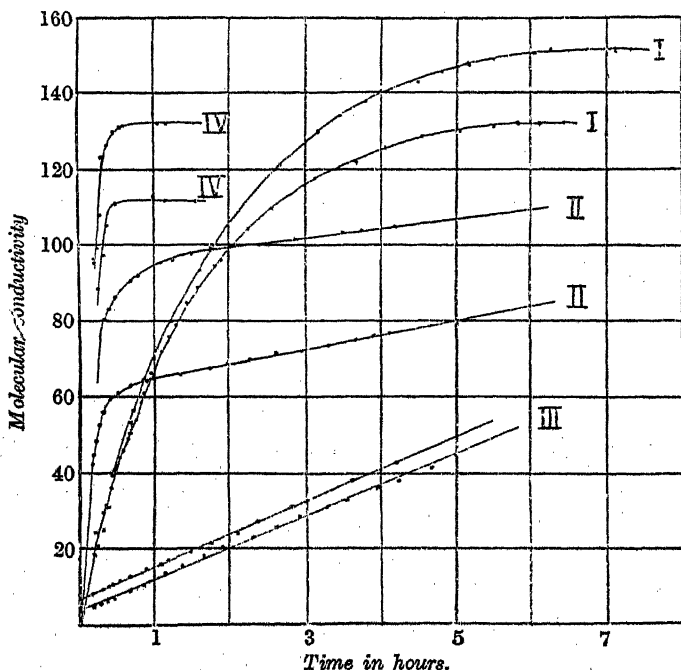
I. 2:4-*Dinitrotoluene.* II. 3:5-*Dinitrotoluene.* III. 2:5-*Dinitrotoluene.* IV. *Dinitrobenzene.* At dilutions $V = 416\cdot2$ and $208\cdot1$ litres.

It was intended to study the dissociation constants of the complete series of isomeric nitro-benzenes and -toluenes with a view to test this hypothesis, but this was found impossible on account of the slow changes in conductivity which occurred on making up the solutions and after each dilution with fresh ammonia. As this change appeared to be associated with the formation and ionisation of an addition compound with ammonia, it was probable that measurements of the rate of change would throw light, not only on the mode of ionisation, but also on the differences between the constitutions of the isomeric dinitrobenzenes. The velocity of

the ionisation process was therefore followed by conductivity measurements. The curves obtained fall into three main groups: (1) those of *m*-dinitrobenzene, and 2:4- and 2:6-dinitrotoluenes, which start from zero conductivity and rise to an equilibrium value with a velocity indicating that the ionisation process follows a monomolecular law (Figs. 1 and 2), (2) those of *o*- and *p*-dinitrobenzenes, and 2:5-, 3:4-, and 2:3-dinitrotoluenes, which show a slight initial conductivity followed by a linear rise, the solutions being initially colourless and becoming yellow as the ionisation process proceeds, and (3) 3:4-dinitrotoluene, which stands by itself in that both of the above types of reaction occur simultaneously.

FIG. 2.
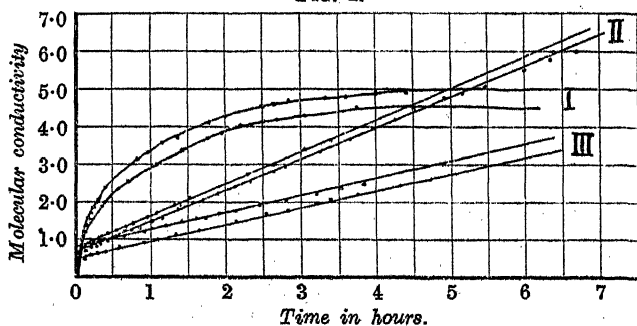
I. 2:6-*Dinitrotoluene*.   II. 3:4-*Dinitrotoluene*.   III. 2:3-*Dinitrotoluene*.

The most striking feature of these results lies in the two distinct ionisation processes which the nitro-compounds undergo in liquid ammonia. The first, represented by equation 1, is characteristic of the *m*-derivatives and is associated with the production of blue or purple colour. The slight initial conductivity of the *o*- and *p*-derivatives in liquid ammonia may be interpreted as being due to a reaction occurring according to equation 1, but if this is the case the intermediate compound must be colourless or present in extremely minute amount.

The second type of ionisation process takes place very slowly with a linear rise in conductivity and is shown mainly by the *o*- and *p*-derivatives. The production of a yellow colour during this change is an indication of the formation of a pseudo-acid with a quinonoid structure, perhaps in the manner

(2) $=NO_2H$ $<NH_2$ NO_2 postulated by Kenner and Burton (J., 1920, **117**, 852) with the formation of substances of the annexed type. This view, however, requires to be tested by further investigation. Both reactions (1) and (2) occur simultaneously in the case of 3:5-dinitrotoluene.
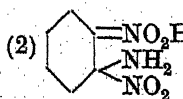
The maximum conductivities due to reaction 1 (Table I) may be regarded as a measure of the degree of ionisation of the nitro-groups and hence of their electronegative character. They have a bearing, therefore, on the problem of the influence of substituents in the benzene ring on the negativity of the nitro-group. The deductions which can be made from the results in this respect are (a) that the nitro-group in a m-position strongly increases the electronegative character of a nitro-group, and (b) that the methyl group increases the negative character of the nitro-group when in the o- and p-position and decreases it when in the m-position. The degree of ionisation of the m-derivatives decreases in the following order : 2 : 4-dinitrotoluene, m-dinitrobenzene, 3 : 5-di-nitrotoluene, and 2 : 6-dinitrotoluene. The last is out of place, being the least instead of the most ionised of the series. The departure from the predicted order could, however, be explained on grounds of steric hindrance by the methyl group, but until the chemical composition of the addition compounds has been investigated it is not profitable to consider such points in detail.

The nature of the parallelism existing between the maximum conductivities and the heats of formation * and melting points of the nitro-compounds will be evident from Table I.

TABLE I.

Nitro-compound.	Colour in liq. ammonia.		Max. mol. cond. due to reaction (1).		Δ μ per hr. Reac-tion (2).		Heat of formn.
	Initial.	Final.	$V=208\cdot1$.	$V=416\cdot2$.		M. p.	Kg.-cal./ gm.-mol.
2 : 4-D.N.T.	Blue	Blue	133	152	0·00	70·5°	+12·2
3 : 5- ,,	Purple	Purple	62	91·5	3·7	92·8	+12·0
2 : 6- ,,	,,	,,	4·5	4·9	0·00	64·3	+10·7
2 : 5- ,,	Colourless	Yellow	3·5	6·5	8·5	51·2	+ 9·8
2 : 3- ,,	,,	,,	0·45	0·7	0·45	59·6	+ 5·4
3 : 4- ,,	,,	,,	0·5	0·7	0·85	58·9	+ 5·1
m-D.N.B.	Blue	Purple	112	132	0·00	90·0	+ 3·0
p- ,,	Colourless	Yellow	0·3	0·75	0·8	171·0	+ 9·9
o- ,,	,,	,,	0·5	1·2	1·0	116·5	− 0·2

EXPERIMENTAL.

Electrolysis of m-*Dinitrobenzene in Liquid Ammonia.*

Materials.—Commercial anhydrous ammonia (99·95%) was em-ployed in the preliminary measurements, and ammonia dried over sodium in the final ones. A quantity of commercial m-dinitro-benzene (m. p. 83°) was crystallised four times from alcohol and then melted at 89°. This specimen was used throughout the experiments.

Solubility.—The solubility of m-dinitrobenzene in liquid ammonia was roughly measured by transferring 10 c.c. of a saturated solution

* Garner and Abernethy, *Proc. Roy. Soc.*, 1921, *A*, **99**, 213.

to a weighed crucible and weighing the residue after evaporation of the solvent. It was approximately 0·8 g. in 100 c.c. The solution is at first blue, but changes in the course of a few minutes to a deep purple. A saturated solution is deep red.

Electrolysis of the Solution.—The electrolysis apparatus consisted of a U-tube, provided with two side tubes for the introduction of ammonia and with platinum wire electrodes at the top of each limb. An additional platinum electrode was sealed into one of the limbs at a point a little above the bend in the U-tube. The U-tube was placed in a cryostat of liquid ammonia which could be maintained at a temperature 1° or 2° lower than that of ammonia boiling under atmospheric pressure. After the introduction of a solution of *m*-dinitrobenzene into the U-tube, the two upper electrodes were connected to a 220-volt circuit. The solution did not boil when the current was passed through it. With commercial ammonia as a solvent, a stream of bubbles appeared at the cathode, and after about ½ hour the liquid around the cathode was quite colourless and was separated from the rest of the solution by a sharp boundary, which moved downwards as the electrolysis proceeded until it reached the bottom of the cathode limb, at which point it remained, however long the electrolysis continued. Simultaneously, a deepening of the colour in the anode limb occurred and a small amount of solid deposit formed on the anode. Solutions of varying concentration, from nearly saturated to very dilute solutions, were thus examined, and in all cases, on complete electrolysis, there was a sharp boundary separating a coloured anode solution from a colourless cathode solution.

Examination of Cathode Solution.—On evaporation, the cathode solution gave no residue, and therefore the kation on discharge does not give rise to a non-volatile product. Since, however, a conducting volatile substance might have been present in the cathode solution, a series of experiments was conducted in which the resistances of the anode and cathode limbs were measured during the electrolysis. The electrolysis was interrupted for a few minutes while these measurements were being made : t = time of electrolysis in hours; R_c and R_a = resistance of cathode and anode solutions, respectively, in ohms; concentration = *ca.* 0·0053 g. of dinitrobenzene in 11 c.c.

$t.$	$R_c.$	$R_a.$	$t.$	$R_c.$	$R_a.$
0	49,030	44,510	61	719,600	31,770
4	63,130	38,320	89	1,371,000	—
30	308,100	35,690	∞	4,770,000	—
51	657,500	34,770			

The resistance of the cathode limb at the end of the electrolysis

was so high as to render it improbable that it contained any substance other than anhydrous ammonia.

With anhydrous ammonia as a solvent, on beginning the electrolysis it was just possible to see tiny bubbles of gas rising from the cathode, but these ceased to form after a minute or two. The amount of gas was certainly much less than would have been anticipated had the nitro-compound combined with the solvent to give rise to an ammonium salt of a pseudo-acid.

If a solution of ammonium chloride in ammonia of half the molecular concentration of the solution of m-dinitrobenzene be electrolysed, a copious stream of hydrogen appears at the cathode, incomparably larger than that from the solution of the nitro-compound.

It can, however, be urged that the hydrogen is used up in reduction of the nitro-compound, but if this were so no gas would be liberated when a small amount of water is present, as in the experiments with commercial ammonia, for this also should be used up in reduction. With regard to this possibility, it should also be mentioned that more than one-third of the nitro-compound is transported from the cathode solution by the current during an experiment. The amount of current thus employed should simultaneously transfer ammonium ions to the cathode and produce sufficient hydrogen to reduce a very large proportion of m-dinitrobenzene, the reduction product of which should be present in the residue after evaporation. Since the solute after the electrolysis melted at 88—89° and consisted almost entirely of unchanged m-dinitrobenzene, reduction, if it occurred at all, could not have occurred to the extent mentioned above. Hence the kation in a solution of m-dinitrobenzene cannot be NH_4.

Conductivities of the Dinitro-benzenes and -toluenes in Liquid Ammonia.

The methods employed in the preparation of anhydrous ammonia and its condensation in the conductivity cell need no special description here, since they were almost identical with those devised by Kraus and Franklin (*Amer. Chem. J.*, 1900, **23**, 277). On a few points of detail their methods were slightly modified. The tap connecting the upper condenser for liquid ammonia with the conductivity cell was completely enclosed by a chamber through which air, dried by passage through liquid air, could be passed continuously. This prevented the intrusion of water through this tap during the mixing of the solute and liquid ammonia. The air regulator of Kraus was replaced by a toluene regulator, which was found to function much better. The temperature of the

cryostat was regulated by controlling the rate of streaming of air through a fine capillary jet. The conductivities were measured by means of an alternating current supplied by a Whetham double rotating commutator and a decade bridge.

Conductivity Measurements with m-*Dinitrobenzene.*—In some of the earlier work considerable difficulties arose due to the slow rate at which the conductivities attained constant values. The measurement of conductivities at a series of dilutions from $V = 60$ to $V = 160,000$ litres per g.-mol. required 20 hours of continuous readings. Also, although the results agreed with those of Kraus up to dilutions of 4,000, at the highest dilutions our results were much higher owing to the entrance of water from the tap above-mentioned and of volatile substances from the phosphoric oxide (even when this had been purified with ozone) used in drying the air by which the liquid was stirred. The best results obtained with this arrangement were as follows, V being the dilution in litres and μ the molecular conductivity :

V	74·67	131·0	230·0	404·0	709·6	1247	2189
μ	86·52	98·24	116·0	134·5	154·7	172·7	189·3
V	3844	6751	11,860	20,830	36,580	64,240	112,800
μ	206·0	236·0	250·9	267·9	279·4	297·0	325·5

These difficulties were overcome after the tap had been modified and the air dried by passage through a coil immersed in liquid air, but the time taken to reach equilibrium was so long in the case of the dinitrotoluenes that it became evident that the method of attack based on determinations of conductivities at each dilution would be extremely laborious. Since measurements of the rate of change of conductivity were likely to produce results of equal value and with less expenditure of effort, this method of investigation was adopted.

Rate of Change of Conductivities with Time.—The nitro-benzenes and -toluenes were kindly supplied to us by Dr. O. L. Brady, either in the pure state or of such a degree of purity that only a few further crystallisations were needed.

Experiments were made on the velocity of ionisation at the dilutions $V = 208·1$ and $416·2$ litres per g.-mol. for each of the nine substances. The requisite quantity of the finely-ground solid was introduced into the bulb of the apparatus. In washing down the solid into the conductivity cell, a portion of the fine light powder was occasionally blown to the top of the bulb, where it was inclined to adhere. This led to a slight source of error in some of the measurements (1 to 2%). As it was only desired to make a preliminary survey of the field, modifications were not made in the apparatus to remove this source of error. The solution was stirred by bubbling

nitrogen through it until no trace of solid could be seen in the cell, and complete solution was ensured by stirring between each of the first half-dozen readings. The cell was then enclosed until the end of the experiment. Readings were thereafter taken over several hours. The moment of introducing the first drop of ammonia into the conductivity vessel was in each case taken as the initial time.

The melting point of the residue after evaporation of the solution after a determination, except in the case of 2 : 4-dinitrotoluene, was never more than about 2° below the melting point of the pure substance. Even the small amount of change which does occur is probably to be accounted for by the action of moisture during the evaporation of the liquid ammonia in the open air. The agreement for duplicate experiments was good, except for 2 : 4-dinitrotoluene, where the velocity of change was subject to fluctuations due to an unknown cause.

In the summary of the results given below, the m-compounds are treated separately, only a few of the experimental readings being given. The others are shown on the curves. The velocity coefficient $k = 1/t \cdot \log_e\{(\mu_0 - \mu_M)/(\mu_t - \mu_M)\}$, where μ_M is the conductivity after equilibrium has been reached. For the highly dissociated nitro-derivatives, the equation gives fairly concordant values for k, but it breaks down for 2 : 6-dinitrotoluene, which is ionised only to the extent of 1—2%. (The conductivity at infinite dilution is about 236 mhos.) It is somewhat surprising that the equation for a reaction of the first order fits so well, especially as the velocity of the back reaction, that of the combination of the ions to give undissociated ammoniate (see equation, p. 1228), has been ignored. The methods adopted in the treatment of simultaneous reactions could be applied here, were the values of x and the numbers of charges on the ions known. Relations based on assumption of simple values for these numbers do not, however, fit the experimental curves.

TABLE II.

m-*Derivatives*.

2 : 6-*Dinitrotoluene.*

$V = 208 \cdot 1$.	t mins.	11	24	54	108	162	
	μ	1·18	1·84	2·68	3·60	4·15	4·5
	k	0·028	0·021	0·017	0·015	0·016	
$V = 416 \cdot 2$.	t mins.	14	20	52	107	171	∞
	μ	1·51	1·90	3·10	4·07	4·53	4·9
	k	0·029	0·025	0·019	0·015	0·015	

3 : 5-*Dinitrotoluene.*

$V = 208 \cdot 1$.	t mins.	12	15	20	25	32	∞
	μ	41·3	48·2	54·4	57·2	59·4	62·0
	k	0·092	0·100	0·105	0·103	0·99	
$V = 416 \cdot 2$.	t mins.	21	24	29	44		∞
	μ	79·2	81·7	84·4	88·2		91·5
	k	0·096	0·093	0·088	0·075		

2 : 4-*Dinitrotoluene.*

$V=208.1$. t mins.	16	27	33	52	95	153	223	∞	
μ	24.6	36.9	43.4	50.5	89.0	110.1	122.1	133.0	
k	0.0128	0.0120	0.0120	0.0119	0.0116	0.0115	0.0126		
$V=416.2$. t mins.	14	31	46	74	97	159	190	249	∞
μ	21.1	42.2	56.8	80.2	93.7	121	130	141	152
k	0.0107	0.0105	0.0102	0.0101	0.0099	0.0100	0.0102	0.0105	

m-*Dinitrobenzene.*

$V=208.1$.	t mins.	10	12	16	22	∞	
	μ	84.3	89.4	98.3	106	112	
	k	0.140	0.133	0.131	0.133		
$V=416.2$.	t mins.	10	13	17	22	24	∞
	μ	96.8	109	118	123	126	132
	k	0.132	0.134	0.132	0.134	0.129	

A summary of the conductivity changes for those substances undergoing ionisation at a constant rate is given in Table III. Of these substances, 3 : 5- and 2 : 5-dinitrotoluene undergo the second type of ionisation at the greatest rate. The constant rate of change is due neither to oxygen nor to catalysis by the walls or platinum electrodes, for the velocities are not influenced when the solution is stirred.

TABLE III.

o- *and* p-*Derivatives* (*including* 3 : 5-*dinitrotoluene also*).

Nitro-compound.	Initial conductivity max. $V=208.1$.	$V=416.2$.	Rate of change per hour (mean).
3 : 5-Dinitrotoluene	133	152	3.7
2 : 5- ,,	3.5	6.5	8.5
2 : 3- ,,	0.45	0.7	0.45
3 : 4- ,,	0.5	0.7	0.85
o-Dinitrobenzene	0.5	1.2	1.0
p- ,,	0.3	0.75	0.8

Summary.

The mechanism of the ionisation of the isomeric dinitro-toluenes and -benzenes in liquid ammonia has been investigated. These nitro-derivatives undergo two distinct types of ionisation, which proceed at measurable velocities. One occurs according to the equation $R(NO_2)_2 + xNH_3 \rightleftharpoons R(NO_2)_2, xNH_3 \rightleftharpoons R(NO_2^{--})_2 + xNH_3^+$, and the other possibly with the production of a pseudo-acid. The former is characteristic of compounds with two nitro-groups in the m-position to one another, and proceeds with a velocity which follows the relation for a reaction of the first order. The addition compound formed from the m-derivatives is blue or purple.

The second type of ionisation process is typical of compounds with the nitro-groups in the o- and p-positions to each other, and proceeds at a rate which is independent of the concentration. 3 : 5-Dinitrotoluene is anomalous in that it shows both types of

change, and the o- and p-derivatives give slight initial conductivities which may be interpreted as due to the first reaction.

The maximum conductivities at any dilution are a measure of the degree of ionisation of the nitro-groups, and hence of their electronegative character. The nitro-groups of the m- are much more negative than those of the o- and p-derivatives. The methyl group in the m-position lowers, and in the o- and p-positions raises, the negative character of the nitro-group. 2 : 6-Dinitrotoluene forms an exception to these rules.

One of us (C. C. S.) wishes to acknowledge the assistance he has received from the Department of Scientific and Industrial Research in carrying out this work.

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CLXVIII.—The Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. Part VII. The Influence of the Phenyl Group on the Formation of the cycloPropene Ring.

By WILHELM HAERDI and JOCELYN FIELD THORPE.

IT is a remarkable fact that the formation of the cyclopropene ring (type II) can be effected with the greatest ease when a mobile hydrogen atom remains in the system produced, that is to say, whenever the ring formed is of the semi-aromatic or glutaconic type, and that when this is not the case it does not appear possible to build up this unsaturated structure. Thus Farmer and Ingold (J., 1923, **123**, 330) found no difficulty in obtaining the acid (II) from α-bromoglutaconic ester (I) and Feist (Ber., 1893, **26**, 750)

$$CH{<}^{CHBrCO_2Et}_{CH \cdot CO_2Et} \qquad CH{<}^{\overset{*}{C}H \cdot CO_2H}_{C \cdot CO_2H} \qquad CMe{<}^{\overset{*}{C}H \cdot CO_2H}_{C \cdot CO_2H}.$$
$$\text{(I.)} \qquad\qquad \text{(II.)} \qquad\qquad \text{(III.)}$$
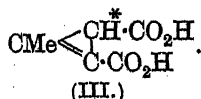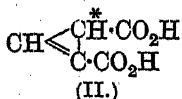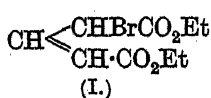
prepared the acid (III) quite easily from bromoisodehydracetic ester. It will be noticed that both of the acids (II) and (III) contain the mobile hydrogen atom, marked *, which enables them to pass into the semi-aromatic form (IV).

$$*(H)CR{<}^{C \cdot CO_2H}_{C \cdot CO_2H} \qquad R{>}C{<}^{CHBr \cdot CO_2Et}_{CHBr \cdot CO_2Et} \qquad R{>}C{<}^{C \cdot CO_2H}_{C \cdot CO_2H}.$$
$$\text{(IV.)} \qquad\qquad\quad \text{(V.)} \qquad\qquad\qquad \text{(VI.)}$$
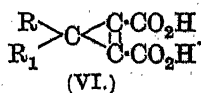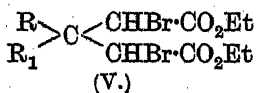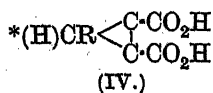
If, however, the conditions are such as to prohibit the existence of this mobile hydrogen within the system, all efforts made to introduce the unsaturated bond into the *cyclo*propane ring fail and in every case the reaction pursues another course. For example (reaction 1), when the dibromo-esters of type (V) lose hydrogen bromide (2 mols.) they do not pass into the acid (VI) or a derivative of it, but yield, in accordance with the value of the group RR_1 and its effect on the carbon tetrahedral angle, either the alkyloxy-derivative (VII), the keto-acid (VIII), or the hydroxy-ring acid (IX).

$$\begin{array}{ccc}
\text{R}\!\!>\!\!\text{C}\!\!<\!\!\begin{array}{l}\text{C(OR)}\!\cdot\!\text{CO}_2\text{H}\\\text{CH}\!\cdot\!\text{CO}_2\text{H}\end{array} & \text{R}\!\!>\!\!\text{C}\!\!<\!\!\begin{array}{l}\text{CO}\!\cdot\!\text{CO}_2\text{H}\\\text{CH}_2\!\cdot\!\text{CO}_2\text{H}\end{array} & \text{R}\!\!>\!\!\text{C}\!\!<\!\!\begin{array}{l}\text{C(OH)}\!\cdot\!\text{CO}_2\text{H}\\\text{CH}\!\cdot\!\text{CO}_2\text{H}\end{array} \\
\text{(VII.)} & \text{(VIII.)} & \text{(IX.)}
\end{array}$$
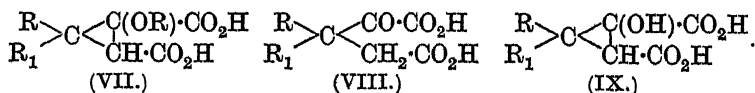
On the other hand (reaction 2), when there exists no tendency to form substances of the above type and when the production of the semi-aromatic system is prohibited, the dibromo-esters undergo fission and yield definite products of degradation. Thus the dibromo-ester (X) yields trimethylacrylic acid (XI) and oxalic acid when treated with potassium hydroxide (Pandya and Thorpe,

$$\text{CMe}_2\!\!<\!\!\begin{array}{l}\text{CHBr}\!\cdot\!\text{CO}_2\text{Et}\\\text{CMeBr}\!\cdot\!\text{CO}_2\text{Et}\end{array} \longrightarrow \text{CMe}_2\!\!\diagdown\!\!\text{CMe}\!\cdot\!\text{CO}_2\text{H} + \begin{array}{l}\text{CO}_2\text{H}\\\text{CO}_2\text{H}\end{array}$$

$$\text{(X.)} \qquad\qquad\qquad\qquad \text{(XI.)}$$
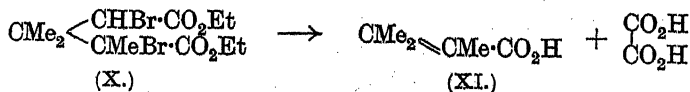
J., 1923, **123**, 2852) and a similar decomposition has recently been recorded in the case of the ββ-dimethyl-α-ethyl derivative (Kon, Smith, and Thorpe, this vol., p. 567).

The object of the experiments described in the present paper was to prepare an acid of formula (XII) which, in its semi-aromatic form, would have the structure (XIII)—in the hope that it would supply further evidence in support of our views regarding the

$$(XII).\quad \text{PhC}\!\!<\!\!\begin{array}{l}\text{CH}\!\cdot\!\text{CO}_2\text{H}\\\text{C}\!\cdot\!\text{CO}_2\text{H}\end{array} \qquad\qquad \text{PhC}\!\!<\!\!_{(H)}\!\!\begin{array}{l}\text{C}\!\cdot\!\text{CO}_2\text{H}\\\text{C}\!\cdot\!\text{CO}_2\text{H}\end{array}\ (XIII.)$$
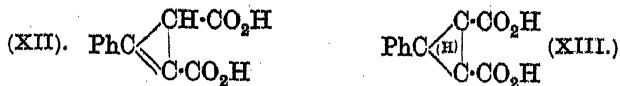
structure of the semi-aromatic ring type of which the acid known as Feist's (III) is at present the best known member. It was expected that the phenyl group in the β-position would confer increased stability on the normal (semi-aromatic) form of the acid as it does in the case of β-phenylglutaconic acid (J., 1912, **101**, 856). Although we were unsuccessful in our attempts to prepare this acid, we, nevertheless, obtained some remarkable evidence on the effect of the phenyl group on three-carbon ring formation.

In the first instance, attempts were made to prepare the acid

(XII or XIII) by the elimination of two molecules of hydrogen bromide from the dibromo-ester (XIV), but the substance underwent both reactions (1) and (2) when treated with alcoholic potassium hydroxide and yielded a result in accordance with the following scheme :

$$\text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CHBr·CO}_2\text{Me}}{\text{CHBr·CO}_2\text{Me}}$$

$$\left.\begin{array}{l}\longrightarrow \text{PhCH:CH·CO}_2\text{H}\\[4pt]\longrightarrow \text{CO}_2\text{H·CO}_2\text{H}\end{array}\right\}10\%$$

$$\longrightarrow \text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{C(OEt)·CO}_2\text{H}}{\text{CH·CO}_2\text{H}}\ 70\%$$

(XIV.)   M. p. 82·5—83·5°.

M. p. 198—199°. (XV.)
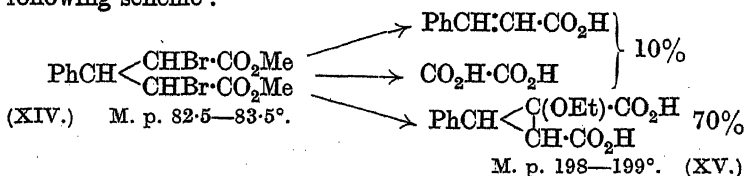
It was then decided to attack the problem by eliminating one molecule of hydrogen bromide from β-bromo-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid (XVI) and an attempt was made to prepare 3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid (XVII) by the elimination of hydrogen bromide from α-bromo-β-phenylglutaric acid (XVIII). The unexpected discovery was then made

$$\text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CBr·CO}_2\text{H}}{\text{CH·CO}_2\text{H}} \qquad \text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CH·CO}_2\text{H}}{\text{CH·CO}_2\text{H}} \qquad \text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CHBr·CO}_2\text{H}}{\text{CH}_2\text{·CO}_2\text{H}}.$$

(XVI.)   (XVII.)   (XVIII.)
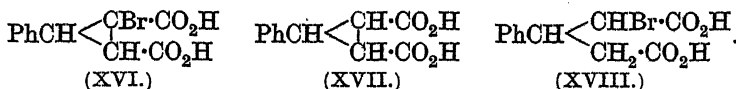
that this bromoglutaric acid (XVIII) contains an active bromine atom and that, in consequence, it is quantitatively converted into β-phenylglutaric acid by potassium hydroxide.

It is very remarkable that the bromine in this compound should also be removed by hot pyridine and that the equations are practic-

$$\text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CHBr·CO}_2\text{Me}}{\text{CH}_2\text{·CO}_2\text{Me}}$$

(XIX.)

$$+\ 3\text{KOH} = \text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CH}_2\text{·CO}_2\text{K}}{\text{CH}_2\text{·CO}_2\text{K}} +\ 2\text{MeOH} + \text{KOBr}$$

$$+\ \text{pyridine} = \text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CH}_2\text{·CO}_2\text{Me}}{\text{CH}_2\text{·CO}_2\text{Me}} + \text{Br}$$
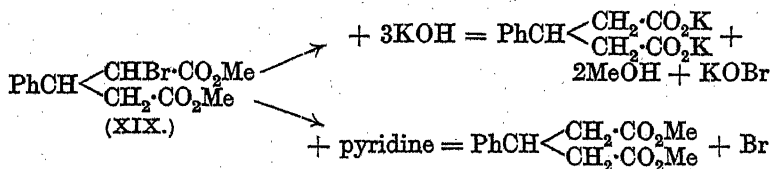
ally quantitative. It has not yet been ascertained what change the pyridine undergoes in this reaction. It is worthy of note that no trace of β-phenylglutaconic acid could be isolated in this way.

Other methods of preparing phenyl*cyclo*propanedicarboxylic acid (XVII) were then investigated and it was ultimately obtained in good quantity by the methods of Buchner (from diazoacetic ester and ethyl cinnamate) and, more readily, by the hydrolysis of ethyl phenyl*cyclo*propanetetracarboxylate (XX) prepared by Kötz and Stahlmann (*J. pr. Chem.*, 1908, 75, 488), in accordance with the scheme :

$$\text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{CH(CO}_2\text{Et)}_2}{\text{CBr(CO}_2\text{Et)}_2} \longrightarrow (\text{XX.}) \quad \text{PhCH}\!<\!\genfrac{}{}{0pt}{}{\text{C(CO}_2\text{Et)}_2}{\text{C(CO}_2\text{Et)}_2} \longrightarrow (\text{XVII.})$$
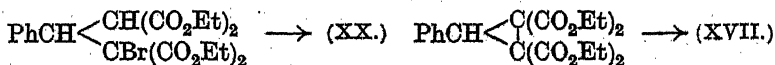
Theoretically the acid (XVII) should exist in three stereochemical modifications, but only one, the *cis-trans* form, has been isolated. This acid can be converted by a special method, described in the experimental part, into the monobromo-ester (XXI), but it was found that this substance also possessed an active bromine atom and that on treatment with potassium hydroxide it was completely converted into the acid (XVII).

$$\text{(XXI.)} \quad \text{PhCH} \diagdown \begin{matrix} \text{CBr·CO}_2\text{Me} \\ \text{CH·CO}_2\text{Me} \end{matrix} \quad \xrightarrow[\longrightarrow]{\text{KOH}} \quad \text{PhCH} \diagdown \begin{matrix} \text{CH·CO}_2\text{H} \\ \text{CH·CO}_2\text{H} \end{matrix} \quad \text{(XVII.)}$$
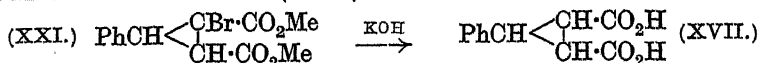
It was then thought that the bromo-derivative of the tricarboxylic acid (XXII) might eliminate hydrogen bromide in the required direction, but it was found that the acid which has been described under this name in the literature and was prepared by Buchner by the hydrolysis of the ester (XXIII) is in reality carboxyphenyl-paraconic acid (XXIV), the hydrolysis of the ester having led to fission of the ring :

$$\text{PhCH} \diagdown \begin{matrix} \text{CH·CO}_2\text{Et} \\ \text{C(CO}_2\text{Et)}_2 \end{matrix} \qquad \text{PhCH} \diagdown \begin{matrix} \text{CH·CO}_2\text{H} \\ \text{C(CO}_2\text{H)}_2 \end{matrix} \qquad \begin{matrix} \text{PhCH—CH·CO}_2\text{H} \\ \text{O·CO·CH·CO}_2\text{H} \end{matrix}$$
$$\text{(XXIII.)} \qquad\qquad \text{(XXII.)} \qquad\qquad \text{(XXIV.)}$$
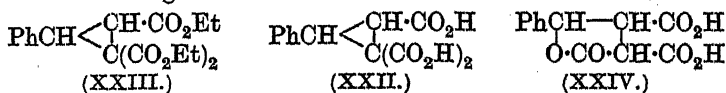
Finally, an attempt was made to prepare the required acid by the hydrolysis of the product formed by the elimination of hydrogen bromide from the ester (XXV). No difficulty was experienced in preparing this bromo-derivative, but it was found to undergo deep-seated decomposition when treated with aqueous potassium hydroxide, the chief product being benzoyl*iso*succinic acid (XXVI) (Bischoff, *Ber.*, 1883, **16**, 1045), which had evidently been formed in accordance with the following scheme :

$$\text{PhC} \diagup^{\text{CH·CO}_2\text{Et}}_{\diagdown \text{CBr(CO}_2\text{Et)}_2} \qquad \text{PhC} \diagup^{\text{C·CO}_2\text{Et}}_{\diagdown \text{OH} \diagdown \text{C(CO}_2\text{Et)}_2}_{\quad\text{H}} \qquad \longrightarrow \qquad \begin{matrix} \text{PhCO·CH·CO}_2\text{H} \\ \text{CH(CO}_2\text{H)}_2 \\ \downarrow \\ \text{Ph·CO·CH}_2 \\ \text{CH(CO}_2\text{H)}_2 \end{matrix}$$
$$\text{(XXV.)} \qquad\qquad\qquad\qquad\qquad \text{(XXVI.)}$$
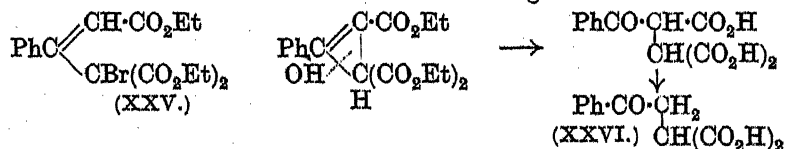
Owing, therefore, to a remarkable series of abnormal reactions the acid (XII) has not yet been obtained, but it is hoped that other experiments which are now in hand will be more successful. The present results are, however, of interest, because they show that the phenyl group, owing doubtless to its marked polar influence, produces effects which are difficult to predict in the present state of our knowledge of these matters.

EXPERIMENTAL.

A. *Derivatives of β-Phenylglutaric Acid.*

β-Phenylglutaric acid was prepared by the condensation of benzaldehyde with ethyl malonate (Knoevenagel, *Ber.*, 1898, **31**,

2591) and the subsequent addition of ethyl sodiomalonate in ethereal solution (Michael, *J. pr. Chem.*, 1887, **35**, 349). The tetracarboxylic ester produced was then hydrolysed by boiling with hydrochloric acid for 20 hours; it was not found necessary to use hydrobromic acid as recommended by Michael (*loc. cit.*).

Methyl α-Bromo-β-phenylglutarate.—β-Phenylglutaric acid (20·8 g.) was treated with phosphorus pentachloride (42 g.), and bromine (18 g.) slowly added to the product, the reaction being completed by warming on the steam-bath for 2 hours. The mixture was poured into methyl alcohol and the ester isolated in the usual manner. On keeping the ester for several days, a small quantity of methyl αα'-dibromo-β-phenylglutarate, m. p. 82·5—83·5° (see below) was deposited. The main portion of the ester did not solidify and was distilled under reduced pressure. The portion boiling at 175—183°/16 mm. gave on redistillation methyl β-phenyl-glutarate, b. p. 180—182°/16 mm., m. p. 86—87°. From the higher-boiling oil a fraction, b. p. 204—206°/17 mm., was isolated; it solidified and on crystallisation from light petroleum or a small quantity of methyl alcohol formed tufts of needles, m. p. 83—83·5°, consisting of *methyl α-bromo-β-phenylglutarate* (Found : Br, 24·45. $C_{13}H_{15}O_4Br$ requires Br, 25·4%). Attempts to isolate the mono-bromo-acid were unsuccessful, because it was always accompanied by the dibromo-compound and the parent acid which prevented it from crystallising. Purification of the acid chloride before bromin-ation (b. p. 171—173°/13 mm.; m. p. 39—40°) is of no advantage.

Methyl αα'-Dibromo-β-phenylglutarate (XIV).—The bromination of β-phenylglutaric acid was carried out in the manner described above, a double quantity of bromine being used; the reaction was complete in about 6 hours. Scarcely any acid ester was formed; the neutral oil solidified on cooling in a freezing mixture, but melted below room temperature. It was purified by dis-tillation under reduced pressure, b. p. 215—220°/20 mm., and solidified in the receiver; on crystallisation from light petroleum or methyl alcohol, short, stout prisms, m. p. 82·5—83·5°, were obtained (Found : Br, 40·4. $C_{13}H_{14}O_4Br_2$ requires Br, 40·6%).

Ethyl αα'-Dibromo-β-phenylglutarate was prepared by pouring the dibromination product into ethyl alcohol and was obtained as a viscid liquid which did not solidify (Found : Br, 37·1. $C_{15}H_{18}O_4Br_2$ requires Br, 37·9%).

Lactone of Ethyl α-Bromo-α'-hydroxy-β-phenylglutarate.—This sub-stance was produced when the dibromo-ethyl ester was distilled under reduced pressure, ethyl bromide being eliminated; it boiled at 230—234°/21 mm. and did not solidify (Found : Br, 25·85. $C_{13}H_{13}O_4Br$ requires Br, 25·6%).

αα'-*Dibromo-*β*-phenylglutaric acid* was obtained by pouring the dibromination product into warm water containing a little hydrobromic acid, the solution being decolorised with animal charcoal and evaporated. On standing for several weeks, short prisms, m. p. 192—193°, were deposited, readily soluble in alcohol and ether, less so in hydrobromic acid (Found : Br, 43·9. $C_{11}H_{10}O_4Br_2$ requires Br, 43·7%).

Hydrolysis of the Bromo-compounds.—1. Fifteen grams of the monobromo-ester dissolved in a little methyl alcohol were added to a boiling solution of 30 g. of potassium hydroxide in 16 c.c. of water, the boiling being continued for 10 minutes. The cooled solution was diluted, the neutral impurities were removed by means of ether, and an excess of dilute sulphuric acid was added, the solution being then extracted with ether. The extract on evaporation gave a brown syrup from which a few crystals separated on keeping; these on crystallisation from benzene formed plates, m. p. 138—139°, and consisted of β-phenylglutaric acid. The remainder of the syrup was esterified with ethyl alcohol, the greater part of the ester boiling at 186—188°/13 mm. and yielding pure β-phenylglutaric acid on hydrolysis with barium hydroxide (Found : C, 63·6; H, 5·8. Calc., C, 63·5; H, 5·8%); the acid was identified by direct comparison with a genuine specimen.

2. The monobromo-ester (6 g.) was boiled for 2 hours with pure pyridine (40 g.), and the mixture was cooled and poured into ice-cold dilute hydrochloric acid; extraction with ether gave an oil which boiled almost completely between 175—185°/16 mm. (3·5 g.), 179—182° on redistillation, and solidified in the receiver; it crystallised from light petroleum in stout prisms, m. p. 86—87°, and consisted of methyl β-phenylglutarate (Found : C, 66·4; H, 6·8. Calc., C, 66·1; H, 6·9%). The fraction boiling above 185° (0·5 g.), which solidified, was the unchanged monobromo-ester.

3. The dibromo-ester (35 g.) was treated with alcoholic potassium hydroxide as described above. On acidifying the reaction product, a small quantity of a very dark oil separated which was removed by filtration; from the clear solution ether extracted 16 g. of a syrup which partially solidified. The solid was freed from oil by means of porous porcelain and fractionally crystallised from ether, benzene, and xylene, when two fractions were obtained. The lower-melting fraction consisted of oxalic acid, which was identified in the usual way (Found : in hydrated form, C, 19·2; H, 4·8. Calc., C, 19·05; H, 4·8%). The higher-melting substance, on crystallisation from ether and light petroleum, formed prisms, m. p. 198—199°, consisting of 2-*ethoxy*-3-*phenyl*cyclopropane-1 : 2-*dicarboxylic acid* (XV) [Found : C, 62·3; H, 5·65;

titration, 13·17 c.c. of $N/20$-NaOH. Ag in silver salt, 47·8. $C_{13}H_{14}O_5$ (dibasic) requires C, 62·4; H, 5·6%; 12·99 c.c. $C_{13}H_{12}O_5Ag_2$ requires Ag, 48·3%). The acid is readily soluble in water, alcohol, or ether, sparingly soluble in benzene or xylene, and insoluble in chloroform or light petroleum; it is stable towards cold alkaline permanganate for more than 24 hours. The *methyl* ester boils at 175—179°/13 mm. (Found: C, 64·85; H, 6·2. $C_{15}H_{18}O_5$ requires C, 64·75; H, 6·5%), and the *ethyl* ester at 184—190°/14 mm. (Found: C, 66·4; H, 6·7. $C_{17}H_{22}O_5$ requires C, 66·6; H, 7·2%). The original acid is obtained by hydrolysing these esters either with potassium hydroxide or with hydrochloric acid.

The porous plates used in the isolation of the ethoxy-acid and oxalic acid were extracted with ether, the recovered syrup was esterified, and the esters were fractionated under reduced pressure. A portion boiled at 110—115°/17 mm., the main fraction at 170—182°/17 mm., and only traces above this temperature. The lowest fraction gave on hydrolysis with 12% sodium hydroxide an acid, forming needles, m. p. 53—54°, consisting of Liebermann's cinnamic acid (Michael, *Ber.*, 1901, **34**, 3655), a mixture of *allo-* and *iso-*cinnamic acids [Found: C, 72·6; H, 5·8; titration, 14·96 c.c. of $N/20$-NaOH. Calc. (monobasic), C, 73·0; H, 5·4%; 14·87 c.c.), which can be separated into two forms, m. p. 63—64° and 54—55°, respectively; the mixture, on treatment with bromine in chloroform, yields αβ-dibromocinnamic acid, m. p. 196—197° (Found: Br, 51·9. Calc., Br, 51·6%). The ester, b. p. 170—182°/17 mm., was hydrolysed and gave the ethoxy-ring acid, m. p. 198—199°.

4. The bromolactonic ester gave the same hydrolysis products as the dibromo-ester, but the yield of cinnamic and oxalic acids increased at the expense of that of the cyclic acid.

B. *Derivatives of 3-Phenylcyclopropane-1 : 2-dicarboxylic Acid.*

3-Phenyl*cyclo*propane-1 : 2-dicarboxylic acid was prepared by Kötz and Stahlmann's method (*loc. cit.*), which was found to be preferable to that of Buchner (*Ber.*, 1888, **21**, 2646); the acid prepared by either method melted at 175—176° and on distillation under reduced pressure gave the anhydride, m. p. 134°.

Monobromination.—*Methyl* 1-*Bromo-3-phenyl*cyclo*propane-1 : 2-dicarboxylate.* The acid (5·5 g.) was converted into the acid chloride by means of phosphorus pentachloride, and 4·8 g. of bromine were slowly added, traces of iodine and iron filings being introduced as catalysts; the temperature was maintained at 120—130° until one-quarter of the bromine had been added, after which the reaction

proceeded spontaneously; scarcely any hydrogen bromide was evolved. On pouring the reaction mixture into ice-cold methyl alcohol, 4·5 g. of a brown powder separated which was collected; on adding water, an oil was precipitated consisting of a neutral (3 g.) and an acid fraction (1 g.). The brown powder was purified by dissolving in benzene and fractionally precipitating with petroleum; all the fractions obtained were, however, amorphous, coloured, and did not possess a definite m. p. The analysis suggested that addition of bromine with fission of the ring had taken place [Found : Br, 38·9 (in light brown sample), 39·25 (in dark brown sample). $C_{13}H_{14}O_4Br_2$ requires Br, 40·6%]. The neutral, oily bromoderivative did not solidify; it contained 36·26% of bromine.

The cyclic acid was brominated in the absence of a catalyst, but in the light of a powerful arc-lamp, the temperature being kept at 125° for ½ hour, then at 140° for ½ hour, and the product was worked up as usual. The acid fraction consisted of the *monobromo-acid* ester, m. p. 175—176° [Found : Br, 26·5; titration, 7·92 c.c. of $N/20$-NaOH. $C_{12}H_{11}O_4Br$ (monobasic) requires Br, 26·7%; 7·45 c.c.) The neutral ester (5·5 g.) was an oil which solidified in a freezing mixture, but melted again at room temperature; it could not be distilled without decomposition (Found : Br, 26·4. $C_{13}H_{13}O_4Br$ requires Br, 25·6%).

The monobromination was also carried out in the absence of a catalyst and without the aid of an arc-lamp, but the products were resinous; the reaction took 4 hours at 100°.

Dibromination.—The acid was dibrominated, an arc-lamp being used to accelerate the reaction; this was complete in 6 hours, the temperature being kept at 130—140°. The reaction product, which was partly resinous, was poured into water and freed from tarry matter by means of animal charcoal. The concentrated solution slowly deposited a small quantity of solid, which was purified by washing with ether, dissolving in alkali and reprecipitating. On crystallisation from much ether, small cubes, m. p. 227—228° (0·3 g.) were obtained (Found : Br, 27·3; titration, 16·5 c.c. of $N/20$-NaOH). These results point to a monobromoacid or a bromolactonic acid [$C_{11}H_9O_4Br$ (dibasic) requires Br, 28·1%; 17·00 c.c. of $N/20$-NaOH].

Hydrolysis of the Bromo-compounds.—The monobromo-ester was hydrolysed exactly as described on p. 1242. On extracting the acidified product with ether and evaporating the extract an oil was obtained which deposited some crystals on standing; these after purification melted at 175—176° and consisted of phenyl-*cyclo*propanedicarboxylic acid. The syrupy portion of the product was esterified with ethyl alcohol and the ester fractionated,

the main portion boiling at 192—205°/16 mm.; this was hydrolysed by means of 12% sodium hydroxide, and the acid so obtained rubbed with a little alcohol. It solidified completely and consisted of the acid, m. p. 175—176°.

The same acid was obtained on hydrolysing the monobromo-ester by means of hot alcoholic potassium hydroxide.

C. *Derivatives of* β-*Phenylglutaconic Acid.*

Phenylpropiolic acid was prepared by Perkin's method (J., 1884, **45**, 172), converted into the ester, b. p. 150—153°/16 mm., by means of alcohol and sulphuric acid, and condensed with ethyl sodiomalonate (Michael, *J. pr. Chem.*, 1895, **49**, 22). The ethyl α-carbethoxy-β-phenylglutaconate so produced could be distilled without decomposition; it yielded β-phenylglutaconic acid, m. p. 154—155°, on hydrolysis with barium hydroxide.

Ethyl α-*Carbethoxy-*α'-*bromo-*β-*phenylglutaconate.*—The tricarb-oxylic ester was brominated under the conditions used by Kötz (*loc. cit.*) in the preparation of β-phenyl*cyclo*propanedicarboxylic acid; 43 g. of bromo-ester were obtained from 33·4 g. of initial material; the crude ester usually contains a slight excess of bromine (Found : Br, 20·0, 22·85, 21·4. $C_{18}H_{21}O_6Br$ requires Br, 19·4%).

Hydrolysis of the Bromo-ester.—The ester (15 g.) was added to a boiling solution of potassium hydroxide (16 g. in 24 c.c. of water), and the mixture boiled for 20 minutes. The cooled mixture was freed from neutral impurities by extraction with ether and gave on acidification a 60—70% yield of benzoyl*iso*succinic acid (XXVI), m. p. 177—178° (Found : C, 59·6; H, 4·75; Ag in silver salt, 50·0; titration, 6·85 c.c. of $N/20$-NaOH. Calc., C, 59·6; H, 4·5; Ag, 49·5%; 6·78 c.c.). The acid on boiling with hydrochloric acid passes into β-benzoylpropionic acid, m. p. 117°. The *ester,* prepared with the aid of sulphuric acid, boils at 185—195°/20 mm. (decomp.), a red coloration being developed; it yields the original acid on hydrolysis with barium hydroxide.

2. The bromo-ester (44 g.) dissolved in a little alcohol was added to a boiling solution of potassium hydroxide (50 g.) in alcohol (100 g.), the mixture boiled under reflux for 35 minutes, then freed from alcohol by evaporation. The residue was dissolved in water, acidified, and extracted with ether, the extract on evaporation yielding a viscous, brown syrup. This was esterified with the aid of sulphuric acid and the mixed esters were fractionated, a small fraction being obtained at 100—168°/16 mm. and a larger one at 170—190°/16 mm.; decomposition and an intense red coloration of the residue were observed towards the end of the distillation. The main fraction gave on redistillation 6 g. of ethyl

β-benzoylpropionate, b. p. 171—173° (Found : C, 69·2 ; H, 6·5. Calc., C, 68·9 ; H, 6·8%). Hydrolysis of the ester with dilute sodium hydroxide gave the corresponding acid, m. p. 116—117° (Found : C, 67·3 ; H, 5·8 ; Ag in silver salt, 37·8. Calc., C, 67·4 ; H, 5·6 ; Ag, 37·9%). The oxime had m. p. 133·5—134·5° (Found : C, 62·3 ; H, 5·8 ; N, 7·4. Calc., C, 62·2 ; H, 5·7 ; N, 7·25%).

3. A similar result was obtained by treating the bromo-ester with methyl-alcoholic potassium hydroxide ; the yield of benzoyl-*iso*succinic acid was somewhat lower.

4. The bromo-ester was kept with the theoretical quantity of alcoholic ammonia for 6 hours, but no reaction occurred ; on standing for 2 days, a substance containing both nitrogen and bromine separated.

Condensation of Ethyl Dibromohydrocinnamate and Ethyl Sodiomalonate.

The condensation was carried out as described by Buchner and Dessauer (*Ber.*, 1892, 25, 1153) for the methyl esters. The mixture of esters obtained was fractionated under 17 mm. pressure, when the following fractions were obtained : (1) 130—165°, 6 g. ; (2) up to 198°, 8 g. ; (3) up to 205°, 6 g. ; (4) up to 215°, 45 g. ; (5) above 215°, 3 g. Fraction (1) consisted of ethyl cinnamate, identified in the form of ethyl dibromohydrocinnamate, m. p. 74—75°, and traces of ethyl malonate. Fractions (2) and (3) partially solidified ; the solid had m. p. 76° after crystallisation and was identified as ethyl ethanetetracarboxylate ; the liquid portion of fraction (2) yielded phenylpropiolic acid, m. p. 136°, on hydrolysis with sodium hydroxide, whilst the liquid portion of fraction (3) gave acetophenone on hydrolysis with hydrochloric acid ; this was probably derived by the decomposition of ethyl benzoylacetate or ethyl ethoxy-cinnamate.

The main fraction boiled at 208—211°/16 mm. on refractionation and consisted of *ethyl phenyl*cyclopropane*tricarboxylate* (XXIII) (Found : C, 64·3 ; H, 6·75. $C_{12}H_{22}O_6$ requires C, 64·7 ; H, 6·95%).

The ester was hydrolysed with alcoholic potassium hydroxide ; the carboxyphenylparaconic acid (XXIV) obtained gradually solidified and was crystallised from ethyl acetate and benzene or petroleum ; it formed prisms, m. p. 88°, which contained four molecules of water of crystallisation. On keeping in a vacuum, the anhydrous form, m. p. 187—188° (decomp.), was obtained ; it can be purified by dissolving in ethyl acetate and gradually evaporating the solvent (Found : C, 57·6 ; H, 4·3. $C_{12}H_{10}O_6$ requires C, 57·6 ; H, 4·0%). On boiling with hydrochloric acid, the acid, m. p. 187—188°, passes into phenylparaconic acid, m. p. 99—100° ; this

acid is also obtained by the direct hydrolysis of the cyclic ester with hydrochloric acid. The elimination of the carboxyl group from the acid, m. p. 187—188°, is, however, best achieved by heating it with twelve times its weight of naphthalene at 185—190° until the evolution of carbon dioxide ceases, the yield of phenylparaconic acid being quantitative. Both acids yield phenyl*iso*crotonic acid on distillation.

The acid, m. p. 187—188° (4 g.), was converted into the acid chloride by means of phosphorus pentachloride, bromine added (2·6 g.), and the brominated acid chloride poured into warm water; after removal of resinous impurities, the solution was evaporated to a small bulk, when colourless prisms, m. p. 99°, of bromophenylparaconic acid separated (Fittig, *Annalen*, 1889, **256**, 76) (Found : Br, 28·3. Calc., Br, 28·1%).

Condensation of Ethyl Dibromocinnamate with Ethyl Sodiomalonate.

(1) With two molecules of sodium ethoxide. The reaction mixture was heated for 25 hours on the steam-bath. The neutral portion of the reaction product was distilled under 17 mm. pressure, and the main fractions were obtained at 110—160° and 160—190°. The lower of these consisted of ethyl ethanetetracarboxylate, m. p. 76°, whilst the liquid consisted of the unchanged bromo-ester. Scarcely any ring compound appeared to be formed.

(2) With one molecule of sodium ethoxide. The reaction was carried out under the same conditions. A high fraction, b. p. 217—219°/18 mm. after redistillation, was isolated. It was free from halogen and reduced permanganate, although it did not react with bromine in chloroform solution (Found : C, 63·6; H, 6·55. $C_{20}H_{26}O_7$ requires C, 63·5; H, 6·9%). On hydrolysis with alcoholic potassium hydroxide the ester yielded an *acid*, m. p. 171—172°, probably containing a lactone ring [Found : C, 60·3; H, 5·0; Ag (in the silver salt), 45·2. $C_{14}H_{12}O_6$ requires C, 60·4; H, 5·0%. $C_{14}H_{10}O_6Ag_2$ requires Ag, 43·9%]. On boiling with hydrochloric acid, the substance passes into phenylparaconic acid; its structure has not yet been determined.

(3) In the absence of alcohol a mixture of ethyl malonate (16 g.) and " molecular " sodium (2·3 g.) in dry ether was kept for 8 hours, ethyl dibromocinnamate (33·5 g.) was then added, and the mixture kept for 2 hours. The esters were isolated and distilled in the usual manner. The main fraction boiled on redistillation at 201—205°/16 mm. and consisted of the ester (XXV) (Found : Br, 18·9. $C_{18}H_{21}O_6Br$ requires Br, 19·4%), whilst the next higher fraction contained less bromine, due to an admixture of ethyl ethanetetra-

U U*

carboxylate, which soon separated in crystals. The ester reduced permanganate, but did not react with bromine in chloroform solution. Several attempts were made to effect ring-closure by the action of finely divided sodium in benzene or toluene, but the ester was recovered unchanged with the exception of a part which resinified. The bromo-ester was then subjected to hydrolysis with 60% potassium hydroxide; the only product isolated was carboxy-phenylparaconic acid, m. p. 187—188° after drying in a vacuum [Found : C, 57·4; N, 4·0; Ag (in the silver salt), 54·7. Calc., C, 57·6; H, 4·0 %. $C_{12}H_9O_7Ag_3$ requires Ag, 55·0%), which yielded phenylparaconic acid on boiling with hydrochloric acid.

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CLXIX.—The Directing Influence of the Methanesulphonyl Group.

By RICHARD FRANCIS TWIST and SAMUEL SMILES.

ACCORDING to Martinet and Haehl (Compt. rend., 1921, 173, 775) the nitration of diphenylsulphone yields the 3 : 3′-dinitro-derivative. This behaviour accords with that of benzenesulphonic acid, which on substitution yields mainly the meta-compounds. It is noteworthy, therefore, that a para-directive influence has been assigned to the methanesulphonyl group of phenylmethylsulphone, which, according to Bourgeois and Abraham (Rec. trav. chim., 1911, 30, 407), yields 4-bromophenylmethylsulphone when treated with bromine in presence of ferric chloride. Further investigation of the matter was needed, for the result of Bourgeois and Abraham indicates the possibility of obtaining the o-disulphonyl group by direct substitution, the process being one which is only seldom realised. Moreover, this apparent difference in character between the sulphonyl or the benzenesulphonyl group and the methane-sulphonyl group, if firmly established, would be of considerable interest in its theoretical aspect. Experiments on the nitration, sulphonation, and bromination of this methylsulphone which have now been made have led only to meta-derivatives, and confirmation of the para-directive influence of the methanesulphonyl group is entirely lacking.

Nitration of phenylmethylsulphone gave a mononitro-derivative, m. p. about 141° (crude), 146° (purified), which was identical with the 3-nitrophenylmethylsulphone (I), m. p. 146°, obtained from the methylation of 3-nitrobenzenesulphinic acid and different from

the 4-nitrophenylmethylsulphone, m. p. 141°, which Zincke (*Annalen*, 1913, **400**, 16) obtained by methylation of 4-nitrobenzenesulphinic acid.

The orientation of the nitration product of phenylsulphoneacetic acid (II) was similar; it was proved by conversion into the methylsulphone.

SO₂Me   SO₂·CH₂·CO₂H   SO₂Me   SO₂Me   SO₂Me

   NO₂   NO₂   SO₂Cl   SMe   SO₂Me

(I.)   (II.)   (III.)   (IV.)   (V.)
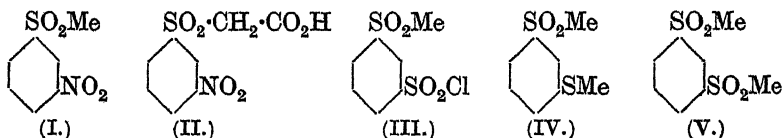
Sulphonation of phenylmethylsulphone also gave the metaderivative (III), the constitution of which was established by conversion through the methyl sulphide (IV) into the dimethylsulphone (V), the latter being identical with the meta-derivative obtained from benzene-*m*-disulphonyl chloride by conversion into the sulphinic acid and subsequent methylation.

Bromination of phenylmethylsulphone by Bourgeois and Abraham's method (*loc. cit.*) led to a substance, m. p. 103°, which was not, as those authors state, 4-bromophenylmethylsulphone, m. p. 103°, but was identical with 3-bromophenylmethylsulphone (VIII), m. p. 103°, which we prepared from 4-bromoaniline-2-sulphonic acid (VII) by eliminating the amino-group and converting the sulphonic acid into the methylsulphone by usual methods. Bourgeois and Abraham prepared 4-bromophenylmethylsulphone by oxidising the corresponding sulphide (VI); we obtained it from 4-bromobenzenesulphinic acid.

SMe   NH₂   SO₂Me

(VI.)   (VII.)   SO₃H   Br   (VIII.)

Br   Br
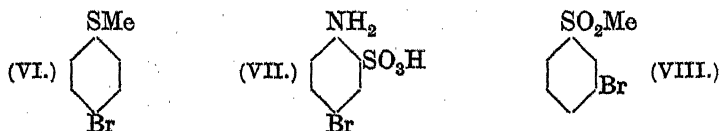
From the comparative state of purity of the crude products of nitration and sulphonation, it seems that appreciable quantities of ortho- or para-compounds are not formed under the conditions adopted.

EXPERIMENTAL.

3 - *Nitrophenylmethylsulphone* (I). — (*a*) From phenylmethylsulphone. Powdered potassium nitrate (1·5 mols.) was slowly added to a stirred solution of phenylmethylsulphone (1 mol.) in six times its weight of cold sulphuric acid. The mixture was kept at 90° for 1 hour, the solid product being then isolated by the addition of water. A further small quantity was removed from

the liquid with ether (yield 96—98%, m. p. 141° approx.). The substance crystallised from hot water in colourless needles, m. p. 146°.

(b) From 3-nitrobenzenesulphinic acid. Limpricht (Ber., 1892, 25, 75, 3477) prepared this acid by reducing 3-nitrobenzene-sulphonyl chloride with sodium sulphite. A purer product is more readily obtained by reduction with a sodium mercaptide according to the scheme $RSO_2Cl + 2R'SNa = (R'S)_2 + RSO_2Na + NaCl$. Powdered 3-nitrobenzenesulphonyl chloride was added in small portions to a warm solution of the requisite amount of the mercaptide in alcohol. When the reaction was complete the sodium chloride was collected and the liquid was evaporated, water being continually added until all alcohol had been expelled. The insoluble disulphide was removed and the sparingly soluble silver sulphinate was obtained from the aqueous liquor. After purification, the silver salt was treated with methyl iodide in the usual manner. The product, 3-*nitrophenylmethylsulphone*, melted after purification at 146°, whether heated alone or mixed with the product obtained by nitration of the sulphone (Found : N, 7·3; S, 15·8. $C_7H_7O_4NS$ requires N, 7·0; S, 15·9%).

For comparison, the 2-nitro- and 4-nitro-derivatives were prepared by methylation of the corresponding sulphinic acids. The melting points (106° and 141°) recorded for these substances in the literature (Claasz, Ber., 1912, 45, 1023; Zincke, Annalen, 1913, 400, 16) were confirmed.

3-*Nitrophenylsulphoneacetic Acid* (II).—The nitration of phenyl-sulphoneacetic acid was conducted as in the case of phenylmethyl-sulphone. After purification from hot water the product had m. p. 62° approx., the exact point of fusion depending on the rate of heating (Found : N, 5·8. Calc., N, 5·7%). Limpricht (*Annalen*, 1897, 294, 243) prepared this substance by oxidation of the corresponding alcohol and recorded m. p. 57°. The acid was heated at 150°, the liberation of carbon dioxide being rapid; the residue, m. p. 146°, was 3-nitrophenylmethylsulphone.

m - *Phenylenedimethylsulphone*   (V). — (a) From benzene - m - disulphonyl chloride. Conversion of this substance into the ammonium disulphinate was effected by Suzuki's method (*J. Coll. Sci. Tokyo*, 1908, 25, xiv, 1). When the silver salt of this sulphinic acid was treated with methyl iodide in boiling methyl alcohol, the required disulphone was obtained. After purification from hot acetic acid it formed colourless prisms, m. p. 196°. Zincke prepared (*Ber.*, 1912, 45, 3471) this substance by oxidising the dimethylthiol and recorded the same melting point.

(b) From phenylmethylsulphone. A solution of phenylmethyl-

sulphone in four times its weight of chlorosulphonic acid was kept at 110—120° for 1 hour. The cooled mixture was poured over ice, and the precipitated oil, which solidified (m. p. 90—91°), crystallised from cold acetone and water, m-*chlorosulphonylphenylmethylsulphone* (III) separating in colourless plates, m. p. 94° (Found : Cl, 14·0; S, 25·4. $C_7H_7O_4ClS_2$ requires Cl, 13·9; S, 25·2%). This sulphonyl chloride was reduced to the mercaptan in the usual manner with excess of tin and hydrochloric acid, the aqueous liquor was removed, and the solid mass of tin and mercaptan extracted with alcohol. From this solution the mercaptan (m. p. 69°) was isolated and converted to the methylthiol (IV) as described below.

This mercaptan was also prepared in the following manner. A solution of the sulphinic acid was obtained by treating the sulphonyl chloride with concentrated aqueous sodium sulphite. The acid was not isolated, but by treatment in this solution at 90° with a little hydrogen iodide in presence of an excess of mineral acid it was converted into the disulphoxide. *Phenylmethylsulphone* m-*disulphoxide*, $(CH_3 \cdot SO_2 \cdot C_6H_4)_2S_2O_2$, was thus obtained in colourless needles, m. p. 200° (Found : C, 41·0; H, 3·4. $C_{14}H_{14}O_6S_4$ requires C, 41·3; H, 3·5%). This disulphoxide was rapidly attacked by boiling aqueous alkali hydroxide, yielding a solution of the alkali sulphinate, whilst the disulphide separated. *Phenylmethylsulphone* m-*disulphide*, $(CH_3 \cdot SO_2 \cdot C_6H_4)S_2$, separated from acetone–water in pale yellow needles, m. p. 120° (Found : C, 44·7; H, 3·7. $C_{14}H_{14}O_4S_5$ requires C, 44·9; H, 3·8%). Hydrolysis of this disulphide by further treatment with boiling aqueous alkali readily furnished a solution of the mercaptide (compare J., 1921, **119**, 1794), from which the mercaptan was obtained in the usual manner.

The mercaptan, prepared by either of these methods, was treated with methyl sulphate in methyl alcohol containing the requisite amount of sodium methoxide. Thus m-*methylthiolphenylmethylsulphone* (IV) was obtained; it separated from light petroleum in colourless plates, m. p. 53° (Found : C, 47·3; H, 4·9. $C_8H_{10}O_2S_2$ requires C, 47·5; H, 5·0%).

Oxidation of the thioether was effected by hydrogen peroxide in warm glacial acetic acid; after purification, the product melted at 196° whether heated alone or with a sample of the material prepared from benzene-m-disulphonyl chloride (Found : C, 41·1; H, 4·2. $C_8H_{10}O_4S_2$ requires C, 41·0; H, 4·3%).

3-*Bromophenylmethylsulphone* (VIII).—(a) By bromination of phenylmethylsulphone. The conditions used were similar to those employed by Bourgeois and Abraham (*loc. cit.*) except that a somewhat higher temperature (130°) was found necessary.

(b) From 3-bromobenzenesulphonic acid. The diazonium salt

obtained from 20 g. of 4-bromoaniline-2-sulphonic acid was decom-
posed by warming the alcoholic solution in presence of a small
quantity of potassium carbonate. When the reacting mixture had
cooled, sodium 3-bromobenzenesulphonate separated; a further
quantity was isolated from the solution (yield, 16 g. of crude
material). The purified sodium salt was converted into the acid
chloride, and the latter was shaken with a concentrated solution
of sodium sulphite. When the chloride had dissolved, the solution
was mixed with an excess of sulphuric acid, the liberated sulphinic
acid being then removed with ether. This acid (m. p. 73°), on
treatment with methyl sulphate in presence of alkali, yielded
3-bromophenylmethylsulphone. A sample of the purified product
melted at 103°, whether heated alone or mixed with the product
yielded by the bromination of phenylmethylsulphone (Found :
C, 35·5; H, 3·1. $C_7H_7O_2BrS$ requires C, 35·7; H, 3·0%).

4-*Bromophenylmethylsulphone* was prepared by the interaction
of sodium 4-bromobenzenesulphinate with methyl sulphate. After
purification, it melted at 103°, but a mixture with an approximately
equal amount of the material obtained by brominating phenyl-
methylsulphone melted indistinctly at about 70° (Found : C, 35·4;
H, 3·0. $C_7H_7O_2BrS$ requires C, 35·7; H, 3·0%). The 4-bromo-
benzenesulphinic acid (m. p. 115°) was prepared from 4-bromo-
benzenesulphonic acid (Nölting, *Ber.*, 1875, **8**, 594; Hübner,
Annalen, 1870, **156**, 326) by usual methods. The substance has
been previously described by Knoevenagel and Kenner (*Ber.*,
1908, **41**, 3323), who obtained it (m. p. 114°) by sulphinating
bromobenzene.

In conclusion, we wish to thank the Department of Scientific
and Industrial Research for a grant which has enabled one of us to
take part in these experiments.

CLXX.—3 : 3-*Diethylpentane* (*Tetraethylmethane*).

By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and ALBERT
E. DUCK.

3 : 3-DIETHYLPENTANE or tetraethylmethane is of special interest
as having the most symmetrical chemical structure (I) of all the
theoretically possible nonanes.

$$C_2H_5\!-\!\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{C}}\!-\!C_2H_5 \quad \text{(I.)}$$
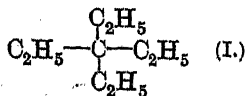
From the general and inorganic point of view the hydrocarbon acquires additional significance owing to the circumstance that it may also be regarded as carbon tetraethyl, being the initial member required to complete the following series :

$$C(C_2H_5)_4, \; Si(C_2H_5)_4, \; Ge(C_2H_5)_4, \; Sn(C_2H_5)_4, \; Pb(C_2H_5)_4.$$
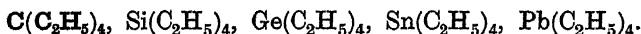
This tertiary paraffin has now been synthesised from diethyl ketone by successive applications of the Grignard and Frankland reactions as summarised in the following scheme :

$$(C_2H_5)_2CO \longrightarrow (C_2H_5)_3C\cdot OH \longrightarrow (C_2H_5)_3CI \longrightarrow C(C_2H_5)_4.$$
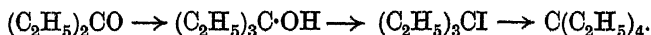
Preparation of 3 : 3-*Diethylpentane.*—Triethylcarbinol, prepared by the Grignard reaction (magnesium ethyl iodide) from diethyl ketone (yield 50%), was saturated with dry hydrogen iodide produced by adding concentrated hydriodic acid to phosphorus tri-iodide (Möslinger, *Annalen*, 1877, **185**, 55; Jourdan, *ibid.*, 1880, **200**, 104), the liquid being cooled to avoid the formation of unsaturated compounds which are formed on raising the temperature. The brown oil was dried and distilled repeatedly under reduced pressure, when *triethylcarbinyl iodide* was obtained as a colourless liquid which rapidly became brown on exposure (Found : I, 55·3. $C_7H_{15}I$ requires I, 56·15%). The yield of purified triethylcarbinyl iodide was 86% : b. p. 71·2°/16 mm.; corrected b. p. (Siwoloboff's method) 153°/737 mm.; $d_4^{20°}$ 1·42.

Zinc ethiodide was prepared by warming ethyl iodide with an equal weight of dry zinc–copper couple made from Kahlbaum's No. 1 zinc and 1·5% aqueous copper sulphate. On heating the ethiodide in a current of carbon dioxide, zinc diethyl distilled and was collected in a reaction flask to which triethylcarbinyl iodide was slowly added at 0°. After several days, the yellowish-white paste was treated successively with cold water and hydrochloric acid. The supernatant oil (48% by weight) from many operations, when tested with bromine water and alkaline permanganate, always showed the presence of unsaturated compounds. Fuming sulphuric acid (60% SO_3), mixtures of nitric and sulphuric acids, and concentrated sulphuric acid were each employed in the removal of unsaturated by-products, and as the best result was obtained with the last of these reagents, the main batch (146 g.) of crude hydrocarbon was shaken with 60% by weight of cold concentrated sulphuric acid and after washing and drying over caustic potash was distilled under reduced pressure. After five fractionations, a product was obtained boiling at 45—47·5°/19 mm. (Found : C, 83·8, 83·7; H, 15·3, 15·5. C_9H_{20} requires C, 84·3; H, 15·7%).

The foregoing processes were found to give the best yields of 3 : 3-diethylpentane, but before this optimum result was attained

the following alternative methods had been tried without success :
(1) magnesium ethyl iodide gave no reaction in the cold with
triethylcarbinyl iodide, and warming led to the formation of
unsaturated products derived from the decomposition of the tertiary
iodide; (2) diethyldichloromethane, prepared from diethyl ketone
and phosphorus pentachloride, when treated with excess of zinc
diethyl at 70°, gave a very poor yield of saturated hydrocarbon;
(3) zinc diethyl was poured into triethylcarbinyl iodide; the reaction
was extremely vigorous and the product was very unsaturated.

Chemical properties. 3 : 3-Diethylpentane did not decolorise
bromine water or alkaline permanganate either in the cold or on
boiling for $\frac{1}{2}$ hour and was not attacked by warm concentrated
sulphuric or nitric acid. In its chemical inertness it showed the
characteristic behaviour of a paraffin.

Physical properties. The hydrocarbon is a clear, colourless
liquid having a faint camphoraceous odour, a property which is
frequently observed in compounds containing a tertiary carbon
atom (Durrans, *Perf. and Essent. Oil Rec.*, 1919, **10**, 104). It was
completely soluble in alcohol and ether, but not so soluble in
alcohol alone.

Melting point. When cooled with a mixture of ether and solid
carbon dioxide, 3 : 3-diethylpentane solidified to a crystalline solid,
which was allowed to melt partly, the liquid being drained away.
This operation was repeated six times until the residue had a constant
melting point, determined by plotting temperature (registered by a
pentane thermometer) against time, both while freezing and melting.
The curves showed a distinct change of slope at $-40°$ to $-42°$,
so that the m. p. is $-41° \pm 1°$.

The portion having the highest melting point was used in deter-
mining the physical properties described below. A specimen which
had not been purified by freezing gave slightly different values;
for instance, the densities showed a difference of one unit in the
third decimal place.

Boiling point (by Siwoloboff's method), correcting for exposed
stem, was $138 \cdot 1°/740$ mm. With further corrections to 760 mm.
at 0°, b. p. $= 139 \cdot 2°/760$ mm.

Density, determined by the pyknometer and compared with
water at 4° :

15°.	20°.	25°.	30°.	40°.
0·75651	0·75222	0·74868	0·74478	0·73758

Hence the coefficient of cubic expansion between 15° and 30° $=$
0·001044.

The molecular volume, V_m, at 15° was $128 \cdot 16/0 \cdot 75651 = 169 \cdot 4$

c.c. The values of the atomic volumes of the constituent elements as given by Traube are C = 9·9 c.c., H = 3·1 c.c. and hence the calculated V_m for 3 : 3-diethylpentane is 151·1 c.c. or the co-volume is 169·4 − 151·1 = 18·3. For monomeric complexity, the normal value of the co-volume is 25·9 c.c., which suggests that the hydrocarbon is associated, the association factor being (25·9−18·3)/ 12·95 = 1·58. But since other physical properties do not indicate association, it is probable that the constitutional effects of symmetrical configuration of the hydrocarbon affect the molecular volume, and for comparison this quantity has been calculated for the other known nonanes, the value of the density being reduced in each case to 15°/4°. The arbitrary coefficient, 0·001031 per 1° for unit density, has been assumed for this purpose.

	d (corr. $\frac{15°}{4°}$).	V_m.	Co-volume.
n-Nonane [4]	0·7213	177·7	26·6
3-Methyloctane [5]	0·7214	177·7	26·6
4-Methyloctane [3]	0·7314	175·2	24·1
2 : 4-Dimethylheptane [2]	0·7200	178·0	26·9
2 : 5-Dimethylheptane [1]	0·7184	178·4	27·3
2 : 6-Dimethylheptane [1]	0·7116	180·1	29·0
2 : 2 : 5-Trimethylhexane [7]	0·7118	180·1	29·0
4-Ethylheptane [6]	0·7445	172·1	21·0
3 : 3-*Diethylpentane*	0·7565	169·4	18·3

[1] Clarke, *J. Amer. Chem. Soc.*, 1912, **34**, 54. [2] *Idem, ibid.*, **34**, 60. [3] *Idem, ibid.*, **34**, 680. [4] *Idem, ibid.*, 1915, **37**, 2536. [5] Hardin, *J. Chim. Phys.*, 1906, **6**, 179. [6] Oberreit, *Ber.*, 1896, **29**, 2003. [7] Kishner, *Abs. Journ. Chem. Soc.*, 1913, **104**, 1164.

2 : 6 - Dimethylheptane and 2 : 2 : 5 - trimethylhexane with terminal *iso-* and tertiary groupings are the least compact. 4-Ethylheptane, on the other hand, with a more symmetrical arrangement of three branching chains, has a much lower molecular volume, whereas in the new isomeride, 3 : 3-diethylpentane with the most symmetrical constitution, V_m is the least of all.

According to Le Bas, " the relative volumes of the atoms remain the same in members of a homologous series although their actual volumes differ from one another." Hence $V_m = nS$, where n is the number of hydrogen equivalents. Thus for 3 : 3-diethylpentane $V_m = 169·41 = 56S$ or $S = 3·0251$, and consequently carbon = 12·10 (since C = 4H). Assuming that the quaternary grouping of $(C_2H_5)_4$ round the central atom has the same value, $V_a(C_2H_5)_4$, in tetraethyl derivatives of other elements of the fourth periodic series, one can calculate the atomic volume of the central atom from $V_m − V_a(C_2H_5)_4$. This assumption may not be strictly valid because the central carbon atom may have a volume different from that of the carbon in the four ethyl groups, but the value for carbon can only be computed from the total number of carbon atoms in

the molecule. However, on this assumption the atomic volumes will have a relative value.

	$d_{4^\circ}^{15^\circ}$ (corr.).	V_m.	Atomic volume of central atom.
$C(C_2H_5)_4$	0·7565	169·4	12·1
$Si(C_2H_5)_4$	0·7903 [1]	182·8	25·5
$Ge(C_2H_5)_4$	0·9980 [6]	189·1	31·8
$Sn(C_2H_5)_4$	{ 1·1898 [2]	197·4	40·1
	{ (1·4089) [3]	(166·7)	(9·4)
$Pb(C_2H_5)_4$	{ 1·6619 [4]	194·5	37·2
	{ 1·62 [5]	199·5	42·2

[1] Mean of Abati and Ladenburg's values. [2] Ghira. [3] Gladstone; this value does not fall into line. [4] Ghira. [5] Burton. [6] Dennis and Hance. References given in table on p. 1259.

When these atomic volumes are plotted against atomic weights, a curve is obtained similar to that given by Le Bas ("Molecular Volumes of Liquid Chemical Compounds," p. 236). This author, who discusses only the data at the melting and boiling points, gives the formula $d_0/d_t = 1 + 0·46 (1 - 273/b. \text{ p.})$ for calculating the molecular volume at the boiling point (P., 1914, **30**, 86).

The density of 3 : 3-diethylpentane at 0° was calculated from its coefficient of expansion and from the above formula at the boiling point, $d = 0·6683$ and $V_m = 191·76$, whilst the calculated volume from the data given by Le Bas for carbon and hydrogen is 206·3. Thus the experimental value indicates a contraction of 14·54.

Vapour density measurements carried out with the Victor Meyer apparatus, using an air jacket regulated to 220°, gave vapour densities of 61·9, 62·0, and 64·4, respectively; mean = 62·8. C_9H_{20} requires 64·1, hence the hydrocarbon is not associated in the vapour state.

Surface tension. The rise of 3 : 3-diethylpentane in a capillary tube was measured over a range of temperatures, the radius of the tube being determined by comparative experiments with pure benzene. The resulting values of the surface tension (γ) and the molecular surface energy ($\gamma V_m^{2/3}$) are given in the following table :

$t.$	20°	25°	30°	40°
γ	22·92	22·45	21·99	21·23
$\gamma V_m^{2/3}$	704·5	692·2	680·4	661·1

The two series of values (γ and $\gamma V_m^{2/3}$) plotted against temperature both give practically straight-line graphs.

In non-associated liquids, the molecular surface energy is a linear function of temperature, the temperature coefficient, k, being a constant of the order of 2·12. The experimental data for this coefficient gave a mean value of $k = 2·17$ between 20° and 40°, leading to the conclusion that 3 : 3-diethylpentane is not associated in the liquid state.

The following hydrocarbons have been investigated previously by the capillary tube method and the results are added for comparison.

Hexane : $\gamma = 18.54$ (8·2°), $\gamma = 13.34$ (62·5°); $k = 2.11$.

n-Octane : $\gamma = 21.31$ (15·5°), $\gamma = 18.56$ (46·3°), $k = 2.217$.

Compressibility of 3 : 3-*diethylpentane.* The compactness of the molecule as deduced from the present evidence is probably connected with the large attraction between the carbon atoms (Richards, *J. Amer. Chem. Soc.*, 1914, **36**, 2438).

Moreover, it appears to be a general rule that the less volatile and more dense of two isomerides has the smaller compressibility, consequently the fact that 3 : 3-diethylpentane has a comparatively high boiling point and the greatest density of the nonanes would indicate that its compressibility would be small.

Refractivity. By means of a Pulfrich refractometer, the refractive index, n, for sodium light at 18° was found to be 1·42057 ; whence $R_L = 43.06$ and $r_G = 71.48$ (calc., 43·53 and 71·79, respectively).

The refractive indices for the other nonanes (Clarke, *J. Amer. Chem. Soc.*, 1912, **34**, 56 ; Kishner, *loc. cit.*) are as follows :

	n_D at 25°.		n_D at 25°.
n-Nonane	1·4125	2 : 5-Dimethylheptane	1·4020
4-Methyloctane	1·4027	2 : 2 : 5-Trimethylhexane	1·3987
2 : 4-Dimethylheptane	1·4014	4-Ethylheptane (at 20°)	1·41564

3 : 3-Diethylpentane, the densest isomeride, has the highest refractive index.

Relationship between Physical Properties and Chemical Structure of 3 : 3-*Diethylpentane and Allied Paraffins.*

The eleven known hydrocarbons containing the quaternary linking, that is, having four radicals attached to one carbon atom, are set out on page 1258. The properties of each compound are compared with those of the normal chain isomerides and the differences in boiling point and density are given under Δ b. p. and Δ d respectively.

The tendency to closer packing is evidenced by the increased density except where the repulsive effect of *iso*-groups at the ends of the chain neutralises this effect, as in II, III, V, and IX. The influence of branch chain configuration on physical properties of hydrocarbons has been studied by L. Clarke (*J. Amer. Chem. Soc.*, 1911, **33**, 523). The more symmetrical grouping, where the chains attached to the central atom are of more equal lengths, increases the density considerably and in such cases the lowering in boiling point is lessened.

		B. p.	Δ b. p.	d (corr. $\frac{15°}{4°}$).	Δ d $\frac{15°}{4°}$.
	C_5H_{12} n-Pentane [1]	36·3°			
I.	2 : 2-Dimethylpropane [5] (Tetramethylmethane)	9·5	−26·8°	—	
	C_6H_{14} n-Hexane [2, 3]	68·9		0·6667	
II.	2 : 2-Dimethylbutane [10, 6] (Trimethylethylmethane)	49·6	−19·3	0·6538	−0·0129
	C_7H_{16} n-Heptane [4, 9]	98·4		0·6885	
III.	2 : 2-Dimethylpentane [11] (Trimethylpropylmethane)	78 (743)	−20·4	0·6776	−0·0109
IV.	3 : 3-Dimethylpentane [8] (Dimethyldiethylmethane)	86—87	−11·9	0·7000	+0·0115
V.	2 : 2 : 3-Trimethylbutane [7] (Trimethylisopropylmethane)	80·75	−17·7	0·6945	+0·0060
	C_8H_{18} n-Octane [13]	124·7		0·7062	
VI.	3-Methyl-3-ethylpentane [12] (Triethylmethylmethane)	118·7 (750)	−6·0	0·7159	+0·0097
VII.	2 : 2 : 3-Trimethylpentane [14] (Trimethyl-sec.-butylmethane)	110·6	−14·1	0·7213	+0·0151
VIII.	2 : 2 : 3 : 3-Tetramethylbutane [16] (Hexamethylmethane)	106	−18·7		
	C_9H_{20} n-Nonane [15]	150·5		0·7213	
IX.	2 : 2 : 5-Trimethylhexane [17] (Trimethylisoamylmethane)	124·5 (763)	−26·0	0·7118	−0·0095
X.	2 : 3 : 3 : 4-Tetramethylpentane (Dimethyldiisopropylmethane)	130	−20·0	—	
XI.	3 : 3-Diethylpentane (Tetraethylmethane)	139·2	−11·3	0·7565	+0·0352

[1] Young, J., 1897, **71**, 446.   [2] *Idem, ibid.*, 1898, **73**, 906.   [3] Francis and Young, J., 1898, **73**, 930.   [4] *Idem, ibid.*, 1898, **73**, 921.   [5] Lwow, Z., 1870, 520.   [6] Van Risseghem, *Bull. Soc. chim.*, 1922, **31**, 62.   [7] Chavanne and Lejeune, *ibid.*, 1922, **31**, 98.   [8] Friedel and Ladenburg, *Annalen*, 1867, **142**, 310.   [9] Thorpe, *ibid.*, 1879, **198**, 364.   [10] Markovnikov, *Ber.*, 1899, **32**, 1445.   [11] *Idem, ibid.*, 1900, **33**, 1908.   [12] Tafel and Jurgens, *ibid.*, 1900, **42**, 2548.   [13] Clarke, *J. Amer. Chem. Soc.*, 1912, **34**, 54.   [14] *Idem, ibid.*, 1912, **34**, 170.   [15] *Idem, ibid.*, 1915, **37**, 2536.   [16] Henry, *Compt. rend.*, 1906, **142**, 1075.   [17] Kishner, *loc. cit.*

The substituted methanes show an increase in boiling point as the methyl groups are successively replaced by the ethyl radical, but the increment diminishes as the replacement progresses :

$C(CH_3)_4$, b. p. 9·5°; $C(CH_3)_3 \cdot C_2H_5$, b. p. 49·6°; $C(CH_3)_2(C_2H_5)_2$, b. p. 86—87°; $C(CH_3)(C_2H_5)_3$, b. p. 118·7°; $C(C_2H_5)_4$, b. p. 139·2°.

Tetraethylmethane having no *iso*-groups, is very compact and

symmetrical.   This is borne out in the high density (it is the most dense of the nonanes) and the comparatively small lowering of the boiling point.

The quaternary grouping when symmetrical has the peculiar effect of restricting the range of liquid existence, as will be seen by a comparison of the melting points and boiling points with those of their normal isomerides.

	M. p.	B. p.
{ n-Pentane	$-130.8°$	$36.3°$
{ 2 : 2-Dimethylpropane	-20	9.5
{ n-Nonane	-51	150.5
{ 3 : 3-Diethylpentane	-41	139.2
{ n-Octane	-57.4	124.7
{ 2 : 2 : 3 : 3-Tetramethylbutane (double quaternary grouping)	$+103—+104$	106

3 : 3-Diethylpentane (Carbon Tetraethyl) compared with its Homologues of the Periodic Group.

The physical properties of the higher members of the following homologous series have only been very incompletely investigated, and the following table shows the changes in melting point, boiling point, density, and refractive index with increase in atomic weight of the central atom.

		M. p.	B. p.	Density.	Ref. index. n_D.
Carbon tetraethyl		$-41°$	$139.2°$	$0.7565 (15°/4°)$	$1.42057 (18°)$
Silicon	,,	$-$	153 [4]	{ $0.8341 (0°)$ [5]	$1.42628 (22.7°)$ [9]
				{ $0.7689 (22.7°/4°)$ [9]	
Germanium	,,	[7] -90	163.5	$0.9911 (24.5°/24.5°)$	$1.407 (18°)$
Tin	,,	$-$	{ 181 [3]	{ $1.18484 (19.1°/4°)$ [8]	{ $1.46835 (19.1°)$ [8]
			{ 175 [6]	{ $1.4089 (t°?)$ [1]	{ $1.5143 (t°?)$ [1]
Lead	,,	$-$	{ >200 [2]	{ $1.64926 (22.4°/4°)$ [6]	$1.51417 (19.1°)$ [8]
			(decomp.)	{ 1.62 [2]	

[1] Gladstone, J., 1891, **59**, 293.   [2] Buckton, *Annalen*, 1859, **109**, 22.
[3] Frankland, *ibid.*, 1859, **111**, 46.   [4] Friedel and Crafts, *ibid.*, 1863, **127**, 31.
[5] Ladenburg, *ibid.*, 1872, **164**, 331.   [6] Pfeiffer and Schnurmann, *Ber.*, 1904, **37**, 320.   [7] Dennis and Hance, *J. Amer. Chem. Soc.*, 1925, **47**, 370.   [8] Ghira, *Gazzetta*, 1894, **24**, i, 309.   [9] Abati, *ibid.*, 1897, **27**, ii, 452.

Materials are being accumulated for a further comparative study of the physical properties of 3 : 3-diethylpentane, its homologues, and its organo-metallic analogues.

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CLXXI.—*The Rotatory Dispersive Power of Organic Compounds. Part XVI. Halogen Derivatives of Camphor. Optical Superposition in the Camphor Series.*

By John Outram Cutter, Henry Burgess, and Thomas Martin Lowry.

1. *Scope of the Experiments.*

The experiments of this series were undertaken with the idea of investigating the influence (i) on the rotatory power of camphor and (ii) on its rotatory dispersion, of the creation of a new asymmetric carbon atom by the introduction of a halogen in the α- or α'-position. Valuable materials for this purpose had been provided by the isolation of a series of α'-derivatives (J., 1915, **107**, 1382; 1922, **121**, 633; 1923, **123**, 1867), with the help of which the influence of the new asymmetric atom could be studied when it is producing a negative instead of a positive effect on the rotatory power. The results of these two lines of investigation are set out in §§ 2 and 3.

2. *Numerical Relations between Rotatory Powers.*

The data summarised in Table I show that

(i) The rotatory power of α- and α'-chlorocamphor can be represented by the formula

$$[\alpha]_{5461} = 65 \cdot 5° \pm 24 \cdot 6° \text{ or } [M]_{5461} = 111 \cdot 8° \pm 41 \cdot 9°,$$

whereas the mean of the rotatory powers of ·camphor and of $\alpha\alpha'$-dichlorocamphor is $[\alpha]_{5461} = 62 \cdot 1°$ or $[M]_{5461} = 113 \cdot 5°$.

(ii) In the same way, the rotatory power of α- and α'-bromocamphor can be represented by the formula

$$[\alpha]_{5461} = 51 \cdot 8° \pm 98 \cdot 9° \text{ or } [M]_{5461} = 111 \cdot 5° \pm 212 \cdot 6°,$$

whereas the mean of the rotatory powers of camphor and of $\alpha\alpha'$-dibromocamphor is $[\alpha]_{5461} = 51 \cdot 3°$ or $[M]_{5461} = 113 \cdot 6°$.

(iii) Again, the rotatory power of $\alpha\beta$- and $\alpha'\beta$-dibromocamphor can be represented by the formula

$$[\alpha]_{5461} = 8 \cdot 8° \pm 91 \cdot 9° \text{ or } [M]_{5461} = 25 \cdot 7° \pm 270°,$$

whereas the mean of the rotatory powers of β-bromocamphor and $\alpha\alpha'\beta$-tribromocamphor * is *about* $[\alpha]_{5461} = 12°$ or $[M]_{5461} = 27°$.

In these three cases, it is possible to recognise the general validity of the idea which forms the basis of van 't Hoff's principle of optical superposition; namely, that the various asymmetric atoms each contribute an independent partial rotation to the observed total

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* The rotatory power of this compound is so small that the mean values would not be affected greatly by the fact that a different solvent, concentration, and temperature were used for measurements of its rotatory power.

rotation of the molecule. Thus in (i), (ii), and (iii) the mean rotations, representing the rotatory power of the camphor nucleus as modified by a halogen atom in the α- or α′-position, have been calculated by two independent methods; the calculated rotations are seen to agree with one another within narrower limits than those imposed by the uncertainty whether specific or molecular rotations should be used in comparing compounds of unequal molecular weight.* A similar statement may be made in reference

TABLE I.

Rotatory Power of Halogen Derivatives of Camphor.

Substance.	Solvent.	Conc. (g./ 100 g.).	$[a]_{5461}$.	$[M]_{5461}$.	Mean.		Diff.
Camphor	Benzene	14·06	52·34°	79·7° ⎫	⎰ [a]	62·1°	19·5°
aa′-Dichloro-camphor *	,,	18·77	71·89	147·3 ⎭	⎱ [M]	113·5	67·6
α-Chlorocamphor	,,	11·09	90·10	153·7 ⎫	⎰ [a]	65·5	49·1
α′- ,,	,,	11·70	40·98	69·9 ⎭	⎱ [M]	111·8	83·8
Camphor	Benzene	14·06	52·34	79·7 ⎫	⎰ [a]	51·3	2·1
aa′-Dibromo-camphor	,,	17·41	50·19	147·6 ⎭	⎱ [M]	113·6	67·9
α-Bromocamphor	,,	14·55	150·71	324·2 ⎫	⎰ [a]	51·8	197·7
α′- ,,	,,	14·50	−47·02	−101·1 ⎭	⎱ [M]	111·5	425·3
β-Bromocamphor	Benzene	33·37	21·50	46·2 ⎫	⎰ [a]	12	20
aa′β-Tribromo-camphor	‖ Acetone †	2·42 §	$[a]_D^{9°}$ 2	$[M]_D$,7·5 ⎭	⎱ [M]	27	39
aβ-Dibromo-camphor	Benzene	16·90	100·64	295·8 ⎫	⎰ [a]	8·8	183·7
α′β-Dibromo-camphor	,,	16·86	−83·11	−244·3 ⎭	⎱ [M]	25·7	540·0
π-Bromocamphor	‡ Chloro-form †	6·32 § $[a]_D^{15°}$ 116		250	—		—
aa′π-Tribromo-camphor	Benzene	2·55 §	91·8	357	—		—
aπ-Dibromo-camphor	,,	15·49	110·83	325·8 ⎫	⎰ [a]	118·7	−15·8
α′π-Dibromo-camphor	,,	6·20	126·63	372·2 ⎭	⎱ [M]	349·0	−46·4

* This specimen was prepared by Mr. H. E. F. Notton.

† We were not able to procure specimens of these two compounds in order to measure their rotatory powers in benzene.

‡ Kipping and Pope (J., 1895, **67**, 382); these authors also give $[a]_D$ = +99·88° for 2·35% in chloroform (*loc. cit.*, p. 379).

§ Grams per 100 c.c. ‖ Armstrong and Lowry, J., 1902, **81**, 1467.

* The practical identity of the *molecular rotations* 147·3° and 147·6° of aa′-dichloro- and aa′-dibromo-camphor, and of the mean molecular rotations 111·8° and 111·5° of the stereoisomeric α- and α′-chloro- and bromo-camphors is very striking and shows that *the influence of the two halogens on the molecular rotatory power of the camphor nucleus is the same*; on the other hand, the *specific rotations* of camphor, 52·3°, α- and α′-bromocamphor, (mean) 51·8°, and aa′-dibromocamphor, 50·2°, are almost equal, although their molecular rotations differ widely.

to the plus or minus influence of the $>$CHBr group in (ii) and (iii). Nothing of the sort can, however, be detected in the π-compounds, where the rotations of the stereoisomerides

$$[\alpha]_{5461} = 118 \cdot 7° \mp 7 \cdot 9°, \ [M]_{5461} = 349 \cdot 0° \mp 23 \cdot 2°$$

differ only to a very small extent from one another, and are actually in the opposite order, for solutions in benzene, to the normal order which they show in chloroform; in addition, the rotations in chloroform of the α- and α'-derivatives, instead of being displaced in opposite directions, are *both* higher than the corresponding value for π-bromocamphor in the same solvent. It is therefore obvious that in the π-derivatives the asymmetric system of camphor has been disturbed in some fundamental way, the nature of which is not yet clear, but may be explored further with the help of the measurements of rotatory dispersion.*

3. *Form of the Dispersion Curves.*

The data shown in Tables III to X all exhibit a complex rotatory dispersion, but in every case except one they can be expressed by two terms of Drude's general equation.† The constants of this equation were calculated directly from the rotation data without regard to any theories as to their relation to the absorption bands of the compound, which were only determined accurately

* This point will be discussed in Part XVII.

† Of the ten cases of complex rotatory dispersion now recorded, *three* are of the type (with two partial rotations of similar sign) which is said by Hunter (J., 1924, 125, 1202) to be "impossible to detect"; *five* more, or one-half of the total, are of the type of which he says that "it will be possible only in rare cases to detect the two terms in the equation"; *one* is too complex to be expressed by a two-term equation; and only *one* is of the totally anomalous type which is described as "the only case in which the form of the dispersion curve may be determined with any degree of confidence." The inaccuracy of these unqualified assertions may be illustrated by the fact that when an attempt was made to fit a one-term equation to the visual readings for α-bromocamphor, the deviation in the calculated value for the last photographic reading, instead of being so small as to be impossible to detect (since the two terms of the equation are of similar sign), amounted to more than half a right angle; and even in the visible region there were systematic deviations which could not have been overlooked by any careful worker. Again, the second type of dispersion, so far from being capable of detection "only in rare cases," is actually the commonest type of all in the camphor series, and may produce even more marked deviations from the requirements of the law of simple rotatory dispersion; thus, in the case of camphor itself, the attempt to fit a simple formula to the visible readings gave rise to an error of more than sixteen right angles in the calculated value corresponding to the last photographic reading (obs. 790°, calc. 2257°, diff. 1467°), although the casual errors were only of the order of about 2°.

at a later stage. The values obtained in this way were as follows :

TABLE II.

Rotatory Dispersion of Halogen Derivatives of Camphor.

	k_1.	k_2.	$\lambda_1{}^2$.	$\lambda_2{}^2$.	$\lambda_1.$ (Å.U.).	$\lambda_a.{}^*$ (Å.U.).
a-Chlorocamphor	+12·938	+ 7·5189	0·09882	0	3140	3050
a'- ,,	+13·733	− 9·401	0·10881	0	3300	3100
a-Bromocamphor	+13·276	+19·530	0·10855	0·0562	3290	3120
a'- ,,	+10·232	−26·393	0·10630	0·03525	3260	3140
β- ,,	+ 9·7419	− 8·1869	0·09915	0	3150	2930
aa'-Dibromocamphor	+14·666	− 8·1713	0·11296	0	3770	3230
aβ- ,,	+16·134	+ 5·8907	0·09863	0	3140	3080
a'β-. ,,	Not expressed by a two-term equation.					
aπ- ,,	+25·163	− 5·741	0·10476	0	3240	3130
a'π- ,,	+34·648	−15·659	0·10470	0	3235	3090

* This column shows the wave-length of maximum absorption of light.

In most cases, the four constants of a two-term equation can be varied to an appreciable extent, in harmony with one another, without introducing any large deviations in the form of the curve,* but this is no longer true of the three-constant equations which (following Drude's usage in the case of quartz) were used in seven out of ten of the above cases; and it is only partly true of the two four-constant equations, since these were based on exceptionally full series of experimental data. This point may be illustrated by referring to the calculation of the formula for the rotatory dispersion of α-bromocamphor in benzene. As originally calculated by us, the constants deduced were as at I below; but, whilst a very close agreement was obtained in the red, yellow, and green regions of the spectrum, nearly all the errors in the violet and ultra-violet regions were negative in sign, although they gave no evidence of " breaking away," since the deviations diminished almost to zero in the last ultra-violet readings, after reaching a maximum of some 2° at about 4000 Å.U. This systematic deviation was corrected † by changing the constants as in II.

	k_1.	k_2.	$\lambda_1{}^2$.	$\lambda_2{}^2$.
I. (Old constants)	13·276	19·428	0·10837	0·05765
II. (New constants)	13·276	19·530	0·10855	0·0562

It will be seen that a very obvious systematic deviation was removed by altering k_2 by 0·1 (a correction of about 1/200), $\lambda_1{}^2$ by 0·00018 (a correction of about 1/600), and $\lambda_2{}^2$ by 0·0014 (a correction of about 1/40). Whilst, therefore, the response of the formula to variations in the different constants is very unequal (*e.g.*, the

* See footnote, Part XV, p. 611.

† We are indebted to Mr. G. O. Owen, B.Sc., for undertaking the calculation of a corrected formula.

formula is far more sensitive to changes in $\lambda_1{}^2$ than in $\lambda_2{}^2$), it looks as if on the average the absolute values of the constants were fixed by the experimental data within perhaps 1%, although in general it is necessary to use four or five significant figures in each constant when calculating the rotations.

A study of the constants leads to the following conclusions.

(a) *The low-frequency term*, which represents the contribution of the ketonic group to the optical activity of the molecule, is always positive, just as in the case of camphor. Its magnitude in the first seven compounds ranged from $k_1 = 10$ to $k_1 = 16$. These values are smaller than those recorded for camphor, but if molecular rotations were used some of them would be larger.

(b) *The high-frequency term*, which can be regarded as representing the sum of the partial rotations of the fixed asymmetric centres, is *negative* in camphor. (i) This term remains negative in β-bromo-camphor and in αα′-dibromocamphor, where no new centre of asymmetry is introduced, and the dispersion is quasi-anomalous (this vol., footnote, p. 608) as in the case of camphor itself. (ii) In the compounds which contain a halogen in the α-position, the large positive partial rotations of the new asymmetric carbon atom make the high-frequency term *positive*, so that the two partial rotations are of similar sign. The rotatory dispersion is therefore complex but normal, and is no longer even quasi-anomalous.*

* In view of Hunter's recommendation that " a return to the older system of classification of rotatory dispersion as normal and anomalous " (which has never been abandoned by us) "is eminently desirable," it is necessary to state clearly that, if it is desired to secure a single rigid method of classifying rotatory dispersions, this system is even more inadmissible on practical grounds than the classification which it is proposed to abandon. Accurate diagnosis on the lines suggested depends on the behaviour of the dispersion curves in the region of long wave-lengths, and is therefore not less, but more, difficult than in the case of simple and complex dispersions, where the diagnosis depends on the behaviour of the curves in the region of shorter wave-lengths. Thus " with the experimental means at present at our disposal " we have no method of following a dispersion curve into the infra-red region in order to test whether it is really normal or anomalous, whereas we can test a simple dispersion experimentally right up to the limit of complete transparency in the ultra-violet, which is also the limit of validity of the formula, and so secure a complete solution of the practical problem of determining (apart from all speculative considerations) whether the rotations obey the law of simple dispersion or not. In practice, therefore, the newer system of classification can be based upon direct experimental measurements in the ultra-violet, whilst the older system of classification rests insecurely upon a process of extrapolation from the visible into the infra-red region of the spectrum. Thus, on the assumption that the two-term equation is valid, we can assert that the dispersion of β-bromocamphor is *complex but normal*, since $k_1 > k_2$ when $\lambda_1{}^2 > \lambda_2{}^2$; but the margin is so narrow that the calculated curve only just fails to cross the axis, and any doubt as to the validity of the

(iii) In the two α′-derivatives, on the other hand, the fixed negative rotation of the camphor molecule is reinforced by the negative partial rotation of the new asymmetric carbon atom. In the case of α′-bromocamphor this reinforcement is sufficient to overbalance the strong positive partial rotation of the ketonic group, with the result that the dispersion curve becomes *totally anomalous*. This case is noteworthy in that *an inflection, maximum* and *reversal of sign* have all been recorded simultaneously in the same solution and in a range of wave-lengths covering only half an octave; the exact positions of these anomalies can be calculated from formulæ given in an earlier paper of this series (J., 1915, **107**, 1197) as follows :

Inflection 5455 Å.U. *Maximum* 4710 Å.U. *Reversal* 3890 Å.U.

(c) In the case of α′β-dibromocamphor, where the influence of the new negative partial rotation is so overwhelming that the total rotations are negative throughout the whole range of the observations, it was no longer possible to make use of a two-term equation, probably because the new fixed partial rotation has a different frequency from the old, so that a three-term equation would be required to express the dispersion.

(d) The π-compounds are seen to be abnormal in several respects, since (i) the low-frequency term is much larger than in any of the other halogen derivatives of camphor; (ii) the high-frequency term is negative in *both* of the stereoisomeric απ- and α′π-dibromo-camphors; (iii) the reversal of asymmetry in the α-carbon atom is compensated, in a manner not hitherto recorded, by a corresponding change in the low-frequency partial rotation, so that the total rotation is scarcely altered by the reversal of the sign of this atom.

4. Relation between Rotatory Dispersion and Absorption.

The publication of the optical rotations now recorded has been held back for more than a year in order to conform to suggestions that the measurements of rotatory dispersion would be of greater value if correlated with measurements of absorption. This correlation was entirely outside the scope of our original programme.

equation would at once make the extrapolation into the infra-red region so uncertain that we could no longer say whether the dispersion should be classed as normal or anomalous. Again, failure to fit a one-term equation in the region of transparency is already sufficient to prove that a dispersion is not simple but complex; and this is still more clearly true when a two-term equation also fails to fit the data, as in the case of α′β-dibromocamphor. The dispersion of this compound is therefore obviously complex; but it cannot be classified with any degree of certainty as normal or anomalous, since the true form of the dispersion equation is still unknown, and it is therefore impossible to say whether the dispersion curve would or would not cut the axis if produced into the region of long wave-lengths.

Moreover, if it had been included, it would probably have led us into serious error, since, if we had started out with the idea that the characteristic wave-length of the rotation constants is identical with the characteristic wave-length of the absorption bands, we should almost inevitably have succumbed to the temptation to adopt the easy method of using the wave-lengths of the absorption bands as constants in the equations of rotatory dispersion, instead of following the more arduous course of deducing these constants from an independent study of the dispersion data. Fortunately, the whole of the dispersion data had been calculated, and the paper had been submitted for publication, before this subtle temptation was presented to us. We can therefore claim without any reservation that the constants of all the dispersion equations given in the present paper are based upon measurements of optical rotations only, and that, as a result of working on this independent basis, we have been led to the discovery of a systematic discrepancy between the values of the characteristic wave-lengths as deduced from the two types of measurement.

A similar discrepancy to that shown in Table II has already been recorded in Part XIII (J., 1924, 125, 2521), where it was shown that the rotation constant of the one-term dispersion equation of camphorquinone gives a characteristic wave-length about 50 Å.U. greater than that of the uncorrected value for the head of the band, and again in Part XV (this vol., p. 611), where the low-frequency partial rotation in the two-term equation for a solution of camphor in benzene is controlled by a dispersion constant of which the characteristic wave-length is about 70 Å.U. greater than that recorded for the head of the absorption band. This difference was, moreover, increased to about 140 Å.U. when the high-frequency dispersion constant was neglected in working out a three-constant equation to express the data for a solution of camphor in *cyclo*hexane.

In the present instance we abandoned the attempt to record the absorption spectra in *benzene* (which had been selected as the best available solvent for the measurements of rotatory dispersion) and deliberately made use of solutions in cyclo*hexane*, the transparency of which enabled us to make the measurements of absorption in the ordinary way, instead of by the precarious use of thin films of concentrated solutions. This change of solvent * had

* Attention has already been directed (Gifford and Lowry, *Proc. Roy. Soc.*, 1923, *A*, 104, 434) to the fact that *cyclo*hexane and benzene differ by less than a degree in their freezing points as well as in their boiling points, a fact which suggests the existence of some analogy of internal structure which is not shown by the conventional classification of the two hydrocarbons as saturated and unsaturated respectively.

already been proved to have no effect on the position of the ketonic band in camphor (Lowry and French, J., 1924, 125, 1924), and we had therefore no reason to suppose that it would affect the position of the band in this series of camphor derivatives.

Table II shows that, if we reserve the case of $\alpha\alpha'$-dibromocamphor for special consideration, the average value of the characteristic wave-length, λ_1, of the low-frequency partial rotation is 3220 Å.U., whilst the average wave-length, λ_a, of the head of the ketonic band is 3080 Å.U. There is therefore a difference of about 140 Å.U. between the two series, just as in the case of camphor in cyclohexane. This discrepancy may again be accounted for by noticing that, when a selective absorption is superposed on a strong general absorption, the observed head of the band will be displaced towards a region of shorter wave-lengths. It is also possible that the omission of the high-frequency dispersion constant in the three-constant equations may tend to increase the value recorded for the low-frequency dispersion constant although the influence of this omission has not yet been studied sufficiently to enable us to draw very definite conclusions in regard to it.* Since, however, these disturbing factors, if operating in the manner suggested, would tend to *increase* the value of λ_1 and to *decrease* the value of λ_a, they would unite in producing discrepancies of the sign actually recorded.† There can therefore be little doubt that the average difference of 140 Å.U. is a fair measure of the effects produced in this way.

Although no great importance can be attached to the study of the individual differences between λ_1 and λ_a, the case of $\alpha\alpha'$-dibromocamphor is sufficiently striking to be picked out from all the others, since an average difference of 140 Å.U. is here increased to more than 500 Å.U. It is noteworthy that the general absorption (which can only be detected with difficulty in the case of camphor) is now so strong that the selective absorption produces little more than a mere " step-out " in the absorption curve, the difference between the maximum and minimum values of $\log \epsilon$ being reduced to 0·1 only, as compared with a value $>1·7$ for a solution of camphor in cyclohexane, where the minimum was not reached at the last recorded wave-length. Although, therefore, the observed head of the ketonic band in $\alpha\alpha'$-dibromocamphor is at a longer wave-length than in any of the other derivatives in the list, we are entitled to suppose that the real maximum of selective absorption would be

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* The average difference in the case of the two four-constant equations of Table II is very nearly equal to the average difference in the case of the seven three-constant equations.

† The sentence " Since . . . direction " in Part XV (this vol., p. 612) in which it is implied that the two errors would tend to cancel out is incorrect and should be deleted.

<div align="center">

TABLE III.

Rotations of α- and α′-Chlorocamphor in Benzene at 20°.

</div>

(a) 11·090 G. of α-chlorocamphor in 100 g. of solution.

(b) 11·6970 G. of α′-chlorocamphor in 100 g. of solution.

Density 0·9018.   Length of tube 6 dcm.

Density 0·90405.   Length of tube 6 dcm.

$[α] = 1·666a.$ $[M] = 1·866[α].$

$[α] = \dfrac{12·938}{λ^2 - 0·09882} + \dfrac{7·5189}{λ^2}.$

$[α] = 1·576a.$ $[M] = 1·866[α].$

$[α] = \dfrac{13·733}{λ^2 - 0·10881} - \dfrac{9·401}{λ^2}.$

Wave-length.	Spec. rot. Obs.	Cal.	Diff.	Obs.	Cal.	Diff.
Li 6707·8	—	—	—	19·3°	19·4°	−0·1°
Cd 6438·5	58·9°	59·1°	−0·2°	22·1	22·2	−0·1
Zn 6362·3	60·9	60·9	±	23·2	23·2	±
Na 5893·0	73·8	73·7	+0·1	30·5	30·5	±
Hg 5790·7	77·3	77·1	+0·2	—	—	—
Cu 5782·2	77·5	77·4	+0·1	31·6	32·8	−1·2
Hg 5780·1	—	—	—	32·9	32·9	±
Hg 5769·6	78·0	77·9	+0·1	—	—	—
Cu 5700·2	80·2	81·7	−1·5	34·5	34·6	−0·1
Hg 5460·7	90·1	90·1	±	41·0	41·0	±
Cu 5218·2	102·6	102·2	+0·4	49·1	49·5	−0·4
Cu 5153·3	106·0	105·9	+0·1	52·1	52·2	−0·1
Cu 5105·5	109·1	108·8	+0·3	54·2	54·4	−0·2
Cd 5085·8	110·0	110·0	±	55·3	55·3	±
Zn 4810·5	130·8	131·2	−0·4	71·5	71·4	+0·1
Cd 4799·9	131·8	131·5	+0·3	72·3	72·1	+0·2
Fe 4762	*133·6*	*134·3*	*−0·7*	—	—	—
Fe 4730	—	—	—	*78·8*	*77·5*	*+1·3*
Zn 4722·2	139·2	137·9	+1·3	77·8	78·5	−0·7
Fe 4548	—	—	—	*94·6*	*94·6*	*±*
Fe 4468	*166·6*	*165·8*	*+0·8*	—	—	—
Fe 4426	—	—	—	*110·3*	*109·7*	*+0·6*
Hg 4358·3	183·2	181·5	+1·7	119·1	119·7	−0·6
Fe 4320	—	—	—	*126·1*	*126·1*	*±*
Fe 4165	*216·6*	*216·6*	*±*			

displaced still further towards the visible region if a correction were made for the influence of the strong general absorption. Even this displacement, however, would probably be insufficient to account for a discrepancy of over 500 Å.U., and we may therefore suspect that the neglect of the high-frequency dispersion constant also produces an exceptionally large effect in this case, perhaps because this constant is unusually large, corresponding with the unusual immanence of the general absorption.

<div align="center">

5. Materials and Measurements.

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(a) α-Chlorocamphor was crystallised five times from benzene and melted at 94°. α′-Chlorocamphor, crystallised twice from alcohol, retained a slight yellow tint; but since its rotatory power was not altered by recrystallisation it was regarded as sufficiently pure for measurements of dispersion; the sample melted at 118°.

TABLE IV.

Rotations of α-Bromocamphor in Benzene at 20°.

14·5480 G. of α-bromocamphor in 100 g. of solution.

Density 0·92770. Length of tube 6 dcm.

$[a] = 1.235a.$ $[M] = 2.311[a].$ $[a] = \dfrac{13.276}{\lambda^2 - 0.10855} + \dfrac{19.53}{\lambda^2 - 0.0562}.$

(a) Visual Readings.				(b) Photographic Readings.			
Wave-length.	Spec. rot. Obs.	Cal.	Diff.	Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	88·57°	88·40°	+0·17°	Fe 5200	172·9°	173·0°	—0·1°
Cd 6438·5	97·79	97·79	±	Fe 5024	191·4	191·6	—0·2
Zn 6362·3	100·78	100·74	+0·04	Fe 4983·3	196·4	196·4	±
Na 5893·0	122·70	122·66	+0·04	Fe 4920·5	203·8	204·2	—0·4
Hg 5790·7	128·44	128·39	+0·05	Fe 4788·7	222·3	222·5	—0·2
Cu 5782·2	128·88	129·88	±	Fe 4632·9	247·0	248·1	—1·1
Hg 5769·6	129·67	129·68	—0·01	Fe 4408·4	296·4	295·8	+0·6
Cu 5700·2	133·88	114·89	—0·01	Fe 4325·8	319·8	381·1·	+1·7
Hg 5460·7	150·71	150·62	+0·09	Fe 4234	345·8	346·5	—0·7
Cu 5218·2	171·45	171·29	+0·16	Fe 4162	369·2	371·7	—2·5
Cu 5153·2	177·85	177·69	+0·16	Fe 4102	395·2	395·8	—0·6
Cu 5105·5	182·59	182·59	+0·30	Fe 4065	413·7	412·8	+0·9
Cd 5085·8	185·92	185·71	+0·21	Fe 4054·9	418·6	417·6	+1·0
Zn 4810·5	219·20	219·27	—0·07	Fe 4001·7	444·6	444·7	—0·1
Cd 4799·9	221·15	221·08	+0·07	Fe 3956·7	469·3	471·1	—1·8
Zn 4722·2	233·08	232·99	+0·09	Fe 3883·3	518·7	519·9	—1·2
Hg 4358·3	309·28	309·73	—0·55	Fe 3852·6	542·1	543·9	—1·8
				Fe 3823	568·1	569·4	—1·3
				Fe 3798·5	591·5	592·4	—0·9
				Fe 3774·8	617·4	616·6	+0·8
				Fe 3758	636·0	635·1	+0·9
				Fe 3753·6	640·9	640·1	+0·8

α-Bromocamphor was crystallised six times from benzene and melted at 76°. β-Bromocamphor was crystallised three times from benzene and melted at 79°; the melting point and rotatory power were unaltered by the last recrystallisation. αα'-Dibromocamphor was crystallised four times from benzene and dried in the dark; this compound is not very stable and readily assumes a yellow colour. Purified specimens of the other five compounds were already available from earlier researches (J., 1922, **121**, 633; 1923, **123**, 1867).

(b) The benzene used as solvent for the first six compounds was purified as described in Part XV. For the remaining four compounds it was purified by a modification of the method of Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825); it was washed free from thiophen with sulphuric acid, then with water, dried over calcium chloride, and frozen four times, the wet setting-point rising during the purification from 5·20° to 5·40°, 5·48°, 5·52° and 5·51°. The last fraction, when dried over sodium, distilled at 80·00—80·03° (uncorr.), and was kept over sodium.

(c) The optical rotations are shown, with calculated values, in Tables III to X. The accuracy of the specific rotations is usually less than that of the original readings, since the reduction factor was generally greater than unity, on account of the low concentration of these solutions, e.g., as compared with the high concentrations which are possible in the case of camphor as a result of its extremely high solubility in organic solvents. In some cases the concentration was limited by the low solubility of one of the two isomerides which it was desired to compare under similar conditions. This limitation does not apply in the case of β-bromocamphor (Table V), the concentration of which was as high as in the case of camphor itself. Attention may perhaps be directed to the large range of readings covered by Tables IV and VI, containing values for 39 and 32 wave-lengths, respectively, to the clearly-seen anomalies of Table V, and to the close concordance with the interpolation formula which is shown by the two long series of 33 readings in Table X.

<center>TABLE V.</center>

<center>*Rotations of* α'-*Bromocamphor in Benzene at* 20°.</center>

<center>14·5020 G. of α'-bromocamphor in 100 g. of solution.</center>

<center>Density 0·92847.   Length of tube 6 dcm.</center>

<center>$[a] = 1·238a.$ $[M] = 2·311[a].$</center>

$$[a] = \frac{10·232}{\lambda^2 - 0·10630} - \frac{26·393}{\lambda^2 - 0·03525}.$$

a) Visual Readings.

Wave-length.	Obs.	Spec. rot. Cal.	Diff.	
Li 6707·8	−33·6°	−33·9°	+0·3°	
Cd 6438·5	−36·2	−36·4	+0·2	
Zn 6362·3	−37·0	−37·1	+0·1	
Na 5893·0	−42·1	−42·1	±	
Hg 5780·1	−43·4	−43·4	±	
Cu 5782·2	−43·3	−43·4	+0·1	
Cu 5700·2	−44·3	−44·3	±	
Hg 5460·7	−47·0	−47·0	±	Inflection.
Cu 5218·2	−49·8	−49·7	−0·1	
Cu 5153·2	−50·5	−50·3	−0·2	
Cu 5105·5	−50·8	−50·8	±	
Cd 5085·8	−50·8	−51·0	+0·2	
Zn 4810·5	−52·7	−52·7	±	
Cd 4799·9	−52·7	−52·8	+0·1	
Zn 4722·2	−52·8	−52·9	+0·1	Maximum.

(b) Photographic Readings.

Fe 4256	−43·3	−44·1	+0·8	
Fe 4090	−30·9	−32·1	+1·2	
Fe 3953	−12·4	−13·3	+0·9	
Fe 3917	− 6·2	− 6·2	±	
Fe 3890	0·00	− 0·1	−0·1	*Reversal.*
Fe 3864	+ 6·7	+ 6·6	+0·1	
Fe 3841	+12·4	+13·1	−0·7	

TABLE VI.

Rotations of β-Bromocamphor in Benzene at 20°.

33·3710 G. of β-bromocamphor in 100 g. of solution.

Density 0·79569.   Length of tube 6 dcm.

$$\lfloor a \rfloor = 0\cdot6277a. \quad [M] = 2\cdot311[a]. \quad [a] = \frac{9\cdot7419}{\lambda^2 - 0\cdot09915} - \frac{8\cdot1869}{\lambda^2}.$$

(a) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	9·5°	9·6°	−0·1°
Cd 6438·5	11·1	10·5	+0·6
Zn 6362·3	11·7	11·7	±
Na 5893·0	15·7	15·7	±
Cu 5782·2	16·9	16·9	±
Hg 5780·1	17·0	17·0	±
Cu 5700·2	17·8	18·0	−0·2
Ag 5468·6	21·4	20·7	+0·7
Hg 5460·7	21·5	21·5	±
Cu 5218·2	26·1	26·2	−0·1
Ag 5209·1	26·2	26·4	−0·2
Cu 5153·3	27·8	27·7	+0·1
Cu 5105·5	29·1	28·9	+0·2
Cd 5085·8	29·4	29·4	±
Zn 4810·5	38·5	38·3	+0·2
Cd 4799·9	38·9	38·7	+0·2
Zn 4722·2	42·2	42·0	+0·2
Hg 4358·3	64·2	64·2	±

(b) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 5268	25·2°	25·2°	±
Fe 4825	37·7	37·7	±
Fe 4571	50·2	49·6	+0·6°
Fe 4424	62·8	62·1	+0·7
Fe 4424	75·3	74·4	+0·9
Fe 4144	87·9	86·8	+1·1
Fe 4054	100·4	99·6	+0·8
Fe 3990	113·0	110·8	+2·2
Fe 3926	125·5	124·0	+1·5
Fe 3874	131·8	133·1	−1·3
Fe 3825	150·7	150·7	±
Fe 3793	163·2	159·7	+3·5
Fe 3758	175·8	179·0	−3·2
Fe 3716	188·3	191·0	−2·7

TABLE VII.

Rotations of αα'-Dibromocamphor in Benzene at 20°.

17·4070 G. of αα'-dibromocamphor in 100 g. of solution.

Density 0·96100.   Length of tube 6 dcm.

$$\lfloor a \rfloor = 0\cdot9963a. \quad [M] = 3\cdot100[a]. \quad [a] = \frac{14\cdot666}{\lambda^2 - 0\cdot11296} - \frac{8\cdot1713}{\lambda^2}.$$

a) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	25·6°	25·4°	+0·2°
Cd 6438·5	29·8	28·9	+0·9
Zn 6362·3	30·1	30·1	±
Na 5893·0	39·6	39·1	+0·5
Cu 5782·2	42·1	41·8	+0·3
Hg 5780·1	42·0	41·9	+0·1
Cu 5700·2	43·8	44·0	−0·2
Hg 5460·7	50·2	51·8	−1·6
Cu 5218·2	61·8	62·0	−0·2
Cu 5153·2	65·2	65·3	−0·1
Cu 5105·5	67·8	67·9	−0·1
Cu 5085·8	69·3	69·1	+0·2
Zn 4810·5	88·5	88·5	±
Cd 4799·9	88·9	88·7	+0·2
Hg 4358·3	149·0	147·5	+1·5

(b) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 4900	79·7°	82·1°	−2·4°
Fe 4690	99·6	99·8	−0·2
Fe 4555	114·6	115·8	−1·2
Fe 4426	134·5	135·2	−0·7
Fe 4328	154·4	154·0	+0·4
Fe 4178	189·3	191·2	−1·9
Fe 4120	199·3	206·8	−7·5
Fe 4046	239·1	239·1	±

TABLE VIII.

Rotations of αβ-Dibromocamphor in Benzene.

16·903 G. of αβ-dibromocamphor in 100 g. of solution.

Density 0·9602.   Length of tube 6 dcm.

$$[a] = 1\cdot0269a. \quad [M] = 3\cdot101[a]. \qquad [a] \quad \frac{16\cdot134}{\lambda^2 - 0\cdot09863} + \frac{5\cdot8907}{\lambda^2}.$$

(a) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	+59·24°	+59·01°	+0·23°
Cd 6438·5	65·24	65·28	—0·04
Zn 6362·3	67·25	67·25	±
Na 5893·0	82·05	81·85	+0·20
Hg 5790·7	85·88	85·73	+0·15
Cu 5782·2	86·17	86·07	+0·10
Hg 5769·6	86·59	86·57	+0·02
Cu 5700·2	89·29	89·42	—0·13
Ag 5465·5	100·44	100·35	+0·09
Hg 5460·7	100·64	100·60	+0·04
Cu 5218·2	114·44	114·53	—0·09
Ag 5209·1	115·42	115·12	+0·30
Cu 5153·2	118·99	118·83	+0·16
Cu 5105·5	122·23	122·17	+0·06
Cd 5085·8	123·85	123·60	+0·25
Zn 4810·5	146·84	146·97	—0·13
Cd 4799·9	148·02	148·02	±
Zn 4722·2	156·05	156·16	—0·11
Zn 4680·1	160·88	160·88	±
Cd 4678·2	160·98	161·11	—0·13
Hg 4358·3	206·62	207·68	—1·06

(b) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 4655	163·8°	163·9°	—0·1°
Fe 4368	205·2	205·9	—0·7
Fe 4312	215·4	216·5	—1·1
Fe 4265	225·6	226·1	—0·5
Fe 4174	245·8	247·3	—1·5
Fe 4135	256·0	257·5	—1·5
Fe 3982	307·5	306·4	+1·1
Fe 3952	317·8	318·1	—0·3
Fe 3928	328·1	328·1	±
Fe 3883	348·6	348·5	+0·1
Fe 3811	388·1	386·7	+1·4
Fe 3795	398·2	397·3	+0·9

TABLE IX.

Rotations of α'β-Dibromocamphor in Benzene.

16·858 G. of α'β-dibromocamphor in 100 g. of solution.

Density 0·9573.   Length of tube 6 dcm.

$$[a] = 1\cdot0327a. \quad [M] = 3\cdot101[a]. \qquad [a] = \frac{-21\cdot4901\lambda^2 - 0\cdot509820}{\lambda^4 - 0\cdot047696\lambda^2 + 0\cdot008542}.$$

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Li 6707·8	—53·68°	—53·70°	+0·02°
Cd 6438·5	58·64	58·64	±
Zn 6362·3	60·34	60·16	—0·18
Na 5893·0	70·68	70·82	+0·14
Hg 5790·7	73·31	73·49	+0·18
Cu 5782·2	73·70	73·65	+0·05
Hg 5769·6	73·98	74·06	+0·08
Cu 5700·2	76·06	75·97	—0·09
Ag 5471·6	82·81	82·77	—0·04
Hg 5460·7	83·11	83·11	±
Cu 5218·2	91·19	91·27	+0·08
Ag 5209·1	91·44	91·59	+0·15

Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Cu 5153·2	—93·42°	—93·63°	+0·21°
Cu 5105·5	95·47	95·41	—0·06
Cd 5085·8	95·91	96·16	+0·25
Zn 4810·5	107·39	107·39	±
Cd 4799·9	108·03	107·86	—0·17
Zn 4722·2	111·38	111·32	—0·06
Cd 4680·1	113·28	113·24	—0·04
Cd 4678·2	113·33	113·33	±
Fe 4448	124·49	124·49	±
Hg 4358·3	129·17	129·12	—0·05
Fe 4251	134·81	134·85	+0·04

TABLE X.

Rotations of αν- and α′π-Dibromocamphor in Benzene.

(a) 15·490 G. of απ-dibromocamphor in 100 g. of solution.

Density 0·9522. Length of tube 6 dcm.

$[\alpha] = 1·1300\alpha.$ $[M] = 3·101[\alpha].$

$$[\alpha] = \frac{25·163}{\lambda^2 - 0·10476} - \frac{5·741}{\lambda^2}.$$

(b) 6·204 G. of α′π-dibromocamphor in 100 g. of solution.

Density 0·9071. Length of tube 6 dcm.

$[\alpha] = 2·9614\alpha.$ $[M] = 3·101[\alpha.].$

$$[\alpha] = \frac{34·648}{\lambda^2 - 0·10470} - \frac{15·659}{\lambda^2}.$$

(a) Visual Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.	Obs.	Spec. rot. Cal.	Diff.
Li 6707·8	+60·67°	+60·13°	+0·54°	+66·00°	+65·56°	+0·44°
Cd 6438·5	67·38	67·38	±	74·06	74·06	±
Zn 6362·3	69·56	69·69	−0·13	76·82	76·78	+0·04
Na 5893·0	87·30	87·23	+0·07	98·11	97·75	+0·36
Hg 5790·7	91·99	92·02	−0·03	104·00	103·54	+0·46
Cu 5782·2	92·11	92·44	−0·33	104·33	104·05	+0·28
Hg 5769·6	92·91	93·06	−0·15	104·66	104·80	−0·14
Cu 5700·2	96·25	96·62	−0·37	109·39	109·14	+0·25
Ag 5468·6	110·39	110·51	−0·12	125·59	125·67	−0·08
Hg 5460·7	110·83	110·83	±	126·63	126·55	+0·08
Cu 5218·2	129·09	129·11	−0·02	148·93	149·22	−0·29
Ag 5209·1	130·01	129·89	+0·12	149·83	150·20	−0·37
Cu 5153·2	134·86	134·86	±	156·45	156·42	+0·03
Cu 5105·5	139·06	139·37	−0·31	162·11	162·09	+0·02
Cd 5085·8	141·69	141·30	−0·21	164·33	164·52	−0·19
Zn 4810·5	173·87	173·87	±	205·82	205·78	+0·04
Cd 4799·9	175·38	175·69	+1·19	208·13	207·70	+0·43
Zn 4722·2	187·20	187·08	+0·12	222·70	222·69	+0·01
Zn 4680·1	193·86	193·96	−0·10	231·58	231·54	+0·04
Cd 4678·2	194·34	194·32	+0·02	232·88	231·97	+0·91
Hg 4358·3	264·79	265·15	−0·36	323·53	323·99	−0·46

(b) Photographic Readings.

Wave-length.	Spec. rot. Obs.	Cal.	Diff.	Wave-length.	Spec. rot. Obs.	Cal.	Diff.
Fe 4294	284·8°	284·9°	−0·1°	Fe 4368	319·9°	320·4°	−0·5°
Fe 4280	290·4	289·5	+0·9	Fe 4261	364·3	364·6	−0·3
Fe 4261	296·1	296·0	+0·1	Fe 4234	377·7	377·3	+0·4
Fe 4122	352·6	352·5	+0·1	Fe 4207	391·0	390·8	+0·2
Fe 4076	375·2	375·5	−0·3	Fe 4152	420·6	421·0	−0·4
Fe 3927	471·2	471·6	−0·4	Fe 4061	479·9	480·4	−0·5
Fe 3900	493·8	493·8	±	Fe 4022	509·5	510·4	−0·9
Fe 3874	516·4	517·0	−0·6	Fe 3986	540·3	540·9	−0·6
Fe 3851	539·0	539·2	−0·2	Fe 3955	570·0	569·8	+0·2
Fe 3809	584·2	584·5	−0·3	Fe 3926	599·6	599·4	+0·2
Fe 3740	674·6	675·5	−0·9	Fe 3899	629·2	629·2	±
Fe 3726	697·2	697·2	±	Fe 3874	658·8	659·2	−0·4

6. Summary.

(a) Measurements have been made of the optical rotations, over a range of wave-lengths, of α- and α′-chlorocamphor, of α, α′-, and β-bromocamphor, and of five isomeric dibromocamphors. Attention is directed to certain regularities in the optical rotations of related

compounds, but the behaviour of the π-derivatives is shown to be altogether exceptional.

(b) In nine cases out of ten, the curves of rotatory dispersion are *complex but normal*, *i.e.*, the rotation increases progressively as the wave-length diminishes, giving rise to quasihyperbolic dispersion curves, which do not exhibit any obvious anomalies; the dispersion is, however, not simple, since it cannot be represented by a single term of Drude's equation.

(c) The dispersion can usually be represented by two terms of the Drude equation; but in the case of α′β-dibromocamphor (where all the rotations are negative) imaginary values are obtained for the constants in such an equation, showing that the dispersions are of still greater complexity.

(d) In the case of α′-bromocamphor the negative term predominates over the positive term in the visible region, but a reversal of sign is observed in the early ultra-violet region; the dispersion is therefore not merely complex but definitely *anomalous*. An inflection at 5455 Å.U., maximum at 4710 Å.U., and reversal of sign at 3890 Å.U. have all been observed experimentally.

CLXXII.—*The Molecular Condition of Phenol in Benzene Solution.*

By JAMES C. PHILIP and C. H. DOUGLAS CLARK.

IN the course of an investigation dealing with the influence of various substances on the solvent power of water (Philip and Bramley, J., 1915, **107**, 377) it was found that the distribution ratio of phenol between water and benzene at 20° was constant over the concentration range studied, *viz.*, up to about 2 grams of phenol per litre of the benzene phase. On the other hand, Rothmund and Wilsmore (*Z. physikal. Chem.*, 1902, **40**, 611), working at 25° and over the concentration range 5·6—50 grams of phenol per litre of the benzene phase, had obtained values of P (= concentration in aqueous phase/concentration in benzene phase) which fell off regularly with increasing concentration. Further work has now

confirmed both the constancy of P at low phenol concentrations and its variation at higher concentrations, the departure from constancy occurring when the amount of phenol per litre of the benzene layer has risen to about 2·8 grams. This constancy of P over a range of concentration is of some interest in connexion with the question of the molecular condition of phenol in benzene solution, as shown below.

EXPERIMENTAL.

Specially purified benzene and phenol were employed in the partition experiments, which were carried out at a constant temperature of 25° in the usual manner. The analytical procedure described in the earlier paper (*loc. cit.*) was tested and found satisfactory.

The results are set out in Table I, in which C_W and C_B represent grams of phenol per litre of the aqueous layer and the benzene layer respectively, whilst $P = C_W/C_B$.

TABLE I.

C_W	0·190	0·395	0·532	0·750	0·930	1·029	1·123
C_B	0·438	0·907	1·245	1·748	2·134	2·378	2·632
P	0·434	0·435	0·427	0·429	0·437	0·433	0·426
C_W	1·354	1·523	1·72	1·87	2·33	2·92	4·62
C_B	3·224	3·63	4·11	4·49	5·57	7·04	11·75
P	0·420	0·420	0·418	0·416	0·418	0·415	0·395
C_W	4·99	9·68	17·0	19·7	23·8		
C_B	12·50	27·4	60·7	77·3	112·7		
P	0·399	0·352	0·280	0·255	0·211		

The values of P obtained by Rothmund and Wilsmore, so far as they fall within the above range of concentration, are somewhat lower than the values recorded in Table I, but fit in generally with the figures there given.

Experiments were made also on the partition of phenol between sodium chloride solutions and benzene, and it appears that the change over from a constant value for P to a variable value occurs at about the same phenol concentration as in the absence of salt.

Discussion of Results.

The fact that the partition coefficient—variable at higher concentrations—becomes constant for values of C_B below about 2·8 proves that in the lowest concentration range the phenol in the benzene solution has reached a steady molecular condition. Since the molecular weight of phenol in water is approximately normal up to fairly high concentrations, the steady condition in question must be that corresponding with simple $C_6H_5\cdot OH$ molecules.

On a first consideration this conclusion may seem to be incon-

sistent with the cryoscopic measurements carried out by many workers. Auwers, for example (*Z. physikal. Chem.*, 1893, **12**, 696), using the freezing-point method, found 145 for the molecular weight of phenol in a benzene solution containing 3 g. of phenol per 1000 g. of benzene, *i.e.*, roughly 2·6 g. per litre of benzene. Whilst, therefore, the partition measurements indicate simple phenol molecules at this concentration, the results of the cryoscopic determinations, as usually interpreted, indicate association to the extent of about 50%.

There appear to be only two possible explanations for this contradiction. First it might be suggested that the presence of water in the partition experiments affects the molecular condition of the phenol, but this explanation must be dismissed, for the depression of the freezing point of benzene caused by the addition of phenol is practically the same whether the benzene is dry or wet. Thus, for example, the depressions observed with solutions of four different concentrations were as follows : (*a*) in absence of water, 0·252°, 0·421°, 0·799°, 1·045°, (*b*) in presence of water, 0·230°, 0·412°, 0·777°, 1·053°.

Secondly, it might be that the high value deduced cryoscopically for the molecular weight of phenol in benzene is due, not to the association of the phenol, but to the separation of a solid solution instead of the pure solid solvent. As a matter of fact, Garelli has proved (*Z. physikal. Chem.*, 1896, **21**, 122) that a solid solution separates when a solution of phenol in benzene begins to freeze. This observation, which does not appear to be generally known, disposes of the contradiction referred to above, and although Garelli considers that association does occur to some extent, the partition experiments now recorded show that association is negligible when the phenol concentration is less than about 2·8 g. per litre of the benzene solution.

In any case it is clearly not permissible, unless with the appropriate corrections, to deduce from cryoscopic data the extent to which phenol is associated in benzene solution, as it undoubtedly is at the higher concentrations. For these cases, however, the degree of association may be calculated from the partition data recorded above, on the following assumptions, (1) that at the higher concentrations the distribution of the simple molecules remains the same as at the low concentrations, (2) that the phenol in the water layer remains in the condition of simple molecules, and (3) that in the more concentrated benzene solutions there is an equilibrium between single and double phenol molecules. It is clear that the figures thus obtained can be only approximate, for on the addition of much phenol the two layers are no longer strictly water and benzene.

In Table II the partition data for the four highest concentrations are set out, along with the values of c_1 and c_2, the calculated molar concentrations of the single and double phenol molecules, respectively, in the benzene phase. From these values of c_1 and c_2 the association factor, A (apparent molecular weight/formula weight), has been deduced for each of the four solutions by the formula $A = (c_1 + 2c_2)/(c_1 + c_2)$.

TABLE II.

C_W.	C_B.	c_1.	c_2.	A.	$c_1{}^2/c_2$.
9·68	27·4	0·24	0·026	1·10	2·21
17·0	60·7	0·42	0·114	1·21	1·55
19·7	77·3	0·49	0·17	1·26	1·44
23·8	112·7	0·59	0·31	1·34	1·14

The values of the association factor A just tabulated are lower than those involved in Bruni's figures for the true molecular weight of phenol in benzene, based on corrected cryoscopic data (*Gazzetta*, 1898, **28**, i, 251), but are fairly consistent with the corresponding figures calculated by Mameli from ebullioscopic measurements (*ibid.*, 1903, **33**, i, 469).

If in the more concentrated solutions there is an equilibrium between single and double molecules, represented by $(C_6H_5 \cdot OH)_2 \rightleftharpoons 2C_6H_5 \cdot OH$, then $c_1{}^2/c_2$ should be a constant. Actually, as shown in the table, the value of $c_1{}^2/c_2$ decreases as C_B increases, hence it is probable that in a concentrated solution of phenol in benzene there are triple molecules as well as double ones (compare Herz, *Ber.*, 1905, **38**, 1138).

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CLXXIII.—*Hepto-* and *Nono-dilactones*.

By GEORGE MACDONALD BENNETT.

THE *spiro*dilactones of ββ'-dihydroxy-diethyl- and -di-*n*-propyl-malonic acids (Leuchs and Gieseler, *Ber.*, 1912, **45**, 2114; Hjelt, *Annalen*, 1883, **216**, 67) are of particular interest in that they are among the simplest known substances which possess potential spiran asymmetry of the type recently realised by Mills and Nodder (J., 1921, **119**, 2094). A crystallographic examination of these two substances has now been made. They crystallise with trigonal and tetragonal symmetry, respectively. A resolution into the optically active forms by simple crystallisation has not been found possible : no enantiomorphism was detected in any crop of crystals obtained in many experiments with various solvents. The nono-

dilactone sometimes crystallises in pseudo-tetragonal form showing supplementary twinning of four biaxial individuals.

The methods of preparation of these two dilactones have been improved. The heptodilactone is easily formed from ethyl ββ′-dimethoxy- and ββ′-dibenzyloxy-diethylmalonate by removal of the methyl or benzyl groups respectively. For the preparation of the benzyloxy-ester, chloroethyl benzyl ether was required. This substance was isolated in an impure condition by Clemo and Perkin (J., 1922, **121**, 642), but has now been obtained pure by a convenient method and should prove to be a valuable synthetic reagent.

The δ-lactone formula $\underset{\text{O}\underline{\hspace{3em}}\text{CO}\frown\text{CO}\underline{\hspace{3em}}\text{O}}{\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2}$ was assigned to the nonodilactone in Richter's "Chemie der Kohlenstoffverbindungen" (11th edn., 1909, p. 576), although the assumption made by Hjelt that his compound was the bis-γ-lactone was reasonable. The presence of the γ-lactone ring in a closely related bromocompound was proved by Leuchs (*loc. cit.*), but direct evidence in the present case had not been produced. It is now shown that potassium hypobromite reacts at once with the dilactone, yielding bromoform. The presence of the group ·CH(OH)·CH₃ in the acid is therefore proved, and Hjelt's formula is confirmed.

EXPERIMENTAL.

Dilactone of ββ′-Dihydroxydiethylmalonic Acid.—Small yields (5—10%) of this substance were isolated from the products of interaction of ethyl malonate with sodium ethoxide and ethylene chlorohydrin, ethylene bromohydrin, chloroethyl acetate, bromoethyl acetate or chloroethyl *p*-nitrobenzoate (2 mols.) in ethylalcoholic solution. Ethyl acetate and ethyl *p*-nitrobenzoate were obtained in good yield in the last two cases, the latter being identified by direct comparison and by the melting point of a mixture with an authentic specimen. The appearance of ring closure by elimination of a molecule of ethyl acetate or ethyl *p*-nitrobenzoate would be remarkable: these substances may, however, have been formed in the alcoholic solution before the condensation occurred.

The dilactone was obtained in poor yield by the action of ethylene chlorohydrin (1 mol.) upon the sodium derivative of ethyl butyrolactonecarboxylate in alcoholic solution (Traube, *Ber.*, 1901, **34**, 1971), and by the use, under similar conditions, of ethylene oxide (2 mols.).* The heptodilactone was also produced in small quantity by the action of an alcoholic solution of sodium ethoxide upon *di-β-chloroethyl malonate*, a colourless liquid, b. p. 164°/15 mm.

* I am indebted to Dr. W. H. Mills, F.R.S., for this suggestion.

(Found : Cl, 30·5. $C_7H_{10}O_4Cl_2$ requires Cl, 31·0%), prepared from malonyl chloride and ethylene chlorohydrin.

Methyl Iodoethyl Ether.—The method of preparation described by Clarke (J., 1912, **101**, 1806) gives but a poor yield and is inconvenient unless an autoclave is used. The replacement of the hydroxyl group of glycol monomethyl ether by means of phosphorus tri-iodide was examined, as a similar reaction had been described for the corresponding ethyl ether by Demole (*Ber.*, 1876, **9**, 746), but the yield of the product was surprisingly low (10%) in spite of repeated experiments and considerable care in the exclusion of moisture and in the purification of the methyl glycol used. The unsatisfactory yield in the preparation of methyl iodoethyl ether makes the isolation of the heptodilactone depending on its use as described below, of little practical value.

Ethyl ββ'-Dimethoxydiethylmalonate.—The crude ester prepared in the usual manner from ethyl malonate and methyl iodoethyl ether (2 mols.) was purified by treatment with potassium hydroxide solution (compare Michael, *J. pr. Chem.*, 1905, **72**, 537). It is a colourless liquid, b. p. 153°/16 mm. (Found : C, 56·4; H, 8·8. $C_{13}H_{24}O_6$ requires C, 56·5; H, 8·8%). It is converted into heptodilactone by boiling for 10 minutes with concentrated hydriodic acid (5 parts), the solution being then diluted, neutralised, boiled for 15 minutes, and again acidified. The dilactone crystallises on cooling (yield 40%).

Benzyl β-Hydroxyethyl Ether.—To an excess of glycol (300 g.) a solution of sodium (37·5 g.) in ethyl alcohol (300 g.) was added and the alcohol distilled off, the last traces being removed by heating at 150° under diminished pressure. Benzyl chloride (225 g.) was gradually added, the reaction being allowed to subside after each addition, and the mixture was heated at 150° for 15 minutes. The oil and sodium chloride were separated by addition of acetone and filtration. The acetone was removed and the greater portion of the glycol recovered by distillation, after which the residue was washed with water, removed in ether, dried over potassium carbonate, and distilled (yield 166 g.).

Benzyl hydroxyethyl ether is a colourless oil, b. p. 138°/15 mm., not miscible with water, but soluble in alcohol and ether (Found : C, 71·0; H, 8·0. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%).

Action of Phosphorus Halides on Benzyl Hydroxyethyl Ether.—When the replacement of the hydroxyl group in the above compound was attempted by means of phosphorus trihalides, unexpected difficulties were encountered as in the case of the corresponding methyl ether. Thus, when benzyl hydroxyethyl ether (40 g.) reacted with phosphorus tribromide (1/3 mol.) in dry benzene

X X*

solution, only 15 g. were obtained of an oil of b. p. 120—130°/20 mm.
which contained the desired benzyl bromoethyl ether together
with some benzyl bromide, whilst a large residue of non-volatile
phosphorus ester remained in the distillation flask. The use of
phosphorus tri-iodide led in the same way to the isolation of a large
proportion of crystalline benzyl iodide (identified by direct com-
parison with a pure specimen) and a small fraction which may have
contained the iodoethyl ether but was insufficient for its complete
isolation.

By means of a reaction described by Darzens (Compt. rend.,
1911, 152, 1314), which has found little application until recently
(e.g., Helferich, Ber., 1921, 54, 1082), an almost quantitative con-
version of the hydroxy-compound into its chloro-derivative is
obtained by a rapid process.

Benzyl Chloroethyl Ether.—The liquid, prepared as described by
Clemo and Perkin (loc. cit.), was a mixture of the chloroethyl ether
with unchanged benzyl alcohol which could not easily be separated.

The pure substance was readily obtained as follows : A mixture
of benzyl hydroxyethyl ether (16 g.) with dimethylaniline (13 g.)
was treated below 30° with thionyl chloride (14·5 g.) dissolved in
chloroform (10 c.c.). The whole was heated on the water-bath
for $\frac{1}{2}$ hour and then poured into dilute hydrochloric acid, the
oil separated in chloroform, the extract washed successively with
dilute acid and water, and distilled. Benzyl chloroethyl ether was
thus obtained (13 g.) as an almost colourless oil of pleasant odour,
b. p. 124°/20 mm., $d_4^{20°}$ 1·109, $n_D^{20°}$ 1·5204 (Found : Cl, 20·65.
$C_9H_{11}OCl$ requires Cl, 20·8%).

$\beta\beta'$-Dibenzyloxydiethylmalonic Acid, $(C_7H_7\cdot O\cdot CH_2\cdot CH_2)_2C(CO_2H)_2$.
—Ethyl malonate was heated for two successive periods of 8 hours
at 100° in alcoholic solution with two quantities of sodium (1 equiv.)
and benzyl chloroethyl ether (1 equiv.). The crude ester was
extracted with potassium hydroxide solution, and hydrolysed by
heating with alcoholic potassium hydroxide solution for 6 hours.
The acid, isolated as a syrup which slowly solidified, crystallised
from benzene–light petroleum in bundles of minute needles, m. p.
120° (Found : C, 67·6; H, 6·6. $C_{21}H_{24}O_6$ requires C, 67·7; H,
6·5%). It gives a sparingly soluble calcium salt and a silver salt
(Found : Ag, 36·6. $C_{21}H_{22}O_6Ag_2$ requires Ag, 36·8%).

The crude ester was converted into the heptodilactone (yield
45—50%) by treatment with fuming hydrobromic acid in the cold
for several days with frequent shaking. The benzyl bromide was
removed in steam, the residue boiled with sodium hydroxide, and
then cooled and extracted once with ether. The aqueous solution
was concentrated and acidified, and the lactone crystallised on

cooling; m. p. 110° (Found : C, 53·8; H, 5·2. Calc., C, 53·8; H, 5·1%).

Dilactone of Dihydroxydipropylmalonic Acid.—Ethyl diallyl-malonate (1 vol.) mixed with sulphuric acid (3 vols. : 70% by weight) was boiled for 3 minutes, diluted with an equal volume of water, and cooled. The dilactone thus obtained was pure after one crystallisation from water; m. p. 106° (Found : C, 58·6; H, 6·55. Calc., C, 58·7; H, 6·5%).

An examination of the mother-liquors in this preparation did not reveal the presence of any other crystalline substance, although three isomerides are conceivable, as with the dibromodilactones of Leuchs and Gieseler (*loc. cit.*).

Action of Potassium Hypobromite on the Nonodilactone.—A mixture of potassium hypobromite solution (8 mols.) with a solution of the pure nonodilactone in potassium hydroxide (2 mols.), when warmed, became turbid and bromoform settled as a heavy oil of b. p. 151°, giving the carbylamine reaction with aniline and sodium hydroxide solution.

Crystallographic Properties of the Dilactones.

Heptodilactone (Bis-γ-butyrolactone-αα-spiran).—The substance crystallises magnificently from acetone, benzene, or water in trigonal crystals having the Millerian axial angle of 127° 18′ (Bravais-Miller axial ratio $a : c = 1 : 2·902$). Forms observed : $c\{111\}$ and $r\{100\}$, the crystals being tabular with c large. Measurements of four selected crystals gave the mean angular values : cr 73° 23′, rr 112° 15′ (calc. 112° 10′). No marked cleavage was observed. The crystals are uniaxial with positive double refraction. Density (by suspension in dense liquids, corr.) $D_4^{16°}$ 1·541. Refractive indices (D line, by immersion in oils) $\omega = 1·552$, $\epsilon = 1·588$.

Nonodilactone (Bis-γ-valerolactone-αα-spiran).—This substance has previously been described (Hjelt, *loc. cit.*) as orthorhombic with $a : b : c = 0·61 : 1 : 0·94$, but the crystals examined were imperfectly developed and only two angles were recorded, measured to the nearest 30′.

In the present investigation well-formed crystals were obtained from solutions in acetone, ethyl alcohol, or ethyl acetate. They are tetragonal, with axial ratios $a : c = 1 : 1·710$. Forms observed : $c\{001\}$, $r\{101\}$, $s\{201\}$ and sometimes $m\{110\}$. Large crystals from acetone showed the above forms equally developed, while crystals from ethyl acetate and ethyl alcohol were tabular with forms c and s only, c being large. Measurements from six crystals gave the mean angular values : cr 59° 41′, cs 73° 37′ (73° 42′), ss 85° 30′ (85° 29′) (calculated values in brackets). Crystals from water

sometimes showed the combination r, s and m. Possibly this was the combination observed by Hjelt, the face he refers to as c being (110). An imperfect cleavage was noticed parallel to a {100}.

Large tabular crystals were usually found to be uniaxial with strong positive double refraction. Density $D_4^{15^\circ}$ 1·321. Refractive indices : $\omega = 1\cdot494$, $\epsilon = 1\cdot571$.

The statement in Hjelt's description that the substance was optically biaxial was accounted for when many small tabular crystals were observed to be twins of four biaxial individuals having a straight extinction and arranged with the acute bisectrix of positive double refraction emerging perpendicular to the basal plane. No sign of the complexity of the whole was detected by examination in ordinary light. Measurements of the optic axial angle (crystals immersed in oil of $n = 1\cdot494$) gave results varying from 8° to 15°, doubtless owing to the difficulty of ensuring the passage of the converging beam of light through one individual alone of so small a complex crystal. It appears improbable that the optical properties of these crystals are the result merely of strain in growth, yet the observation of Martin (*Neues Jahrb. Min.*, 1891, **7**, 1) in a similar case, that minute crystals as first deposited from solution were uniaxial, has been confirmed with this substance.

My thanks are due to Miss E. M. Whincop for help with some of the experiments above described, and to the Chemical Society for assistance in the purchase of materials.

CLXXIV.—*Semicarbazones of Benzoin.   Part I.*

By ISAAC VANCE HOPPER.

BILTZ and his co-workers (*Annalen*, 1905, **339**, 243) have examined the action of semicarbazide on benzoin, benzil, and related compounds. They found—and this has been confirmed by the present work—that the benzoinsemicarbazone (I) formed by interaction of benzoin and semicarbazide hydrochloride in aqueous-alcoholic solution was accompanied by the by-products diphenylhydroxy-triazine (II; keto-form) and diphenyliminazolone (III).

PhC:N·NH——CO   PhC:N·NH   PhC·NH   PhC:N·NH·CO
PhCH·OH H₂N   PhC:N·CO   PhC·NH ⟩CO   PhCO   H₂N
   (I.)   (II.)   (III.)   (IV.)
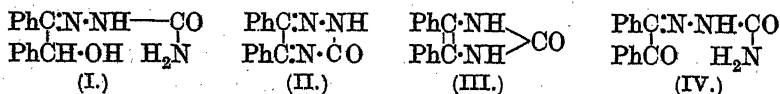
Biltz proved that oxidation of a part of the benzoin or benzoinsemi-

carbazone to benzil or benzilsemicarbazone, followed by loss of water from the last-mentioned compound through intramolecular condensation, gave rise to (II), but his explanation of the mechanism of this oxidation and of the formation of (III) is unsatisfactory.

The presence of ammonia in the spent liquors and of (II) and (III) as by-products (see also Biltz, *loc. cit.*) suggests to the author that benzoin can react with semicarbazide after the fashion of α-hydroxy-ketones and phenylhydrazine, yielding a derivative of the corresponding diketone, the oxidation of the secondary alcoholic group being effected by semicarbazide, which is thereby reduced to ammonia and carbamide, the latter of which condenses with unchanged benzoin (acting as αβ-dihydroxystilbene) to form diphenyliminazolone :

$(I) + NH_2 \cdot NH \cdot CO \cdot NH_2 \longrightarrow (IV) + NH_3 + (NH_2)_2CO ;$

$(IV) \longrightarrow (II) + H_2O ; \quad PhCH(OH) \cdot COPh \longrightarrow PhC(OH){:}C(OH)Ph$
$\xrightarrow{CO(NH_2)_2} (III) + 2H_2O.$
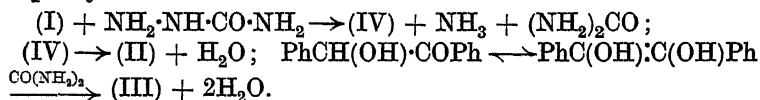
Benzoin has been condensed with carbamide in alcoholic solution (Anschutz, *Annalen*, 1891, **261**, 129; 1894, **284**, 8) and in acetic acid solution (Biltz and Stellbaum, *ibid.*, 1905, **339**, 264) to give good yields of diphenyliminazolone. Incidentally there is strong evidence here that benzoin can behave in a dienolic form. The formation of (II) precludes the formation of benzildisemicarbazone and also accounts for the absence of benzilmonosemicarbazone from the reaction products.

Benzoin and δ-benzylsemicarbazide hydrochloride in aqueous-alcoholic solution reacted in a similar manner. In this case, however, the presence of the benzyl radicle in the δ-position of the semicarbazide residue inhibited hydroxytriazine formation, and the chief product of the reaction was benzildibenzylsemicarbazone (VII); a little benzilmonobenzylsemicarbazone (VI) and varying amounts of benzoinbenzylsemicarbazone (V) were also obtained.

$$\begin{array}{ccccc} PhCH \cdot OH & \xrightarrow{NH_2 \cdot NH \cdot A} & PhCO & \xrightarrow{NH_2 \cdot NH \cdot A} & PhC{:}N \cdot NH \cdot A \\ PhC{:}N \cdot NH \cdot A & & PhC{:}N \cdot NH \cdot A & & PhC{:}N \cdot NH \cdot A \\ (V.) & & (VI.) & & (VII.) \end{array}$$

$$[A = CO \cdot NH \cdot CH_2Ph]$$
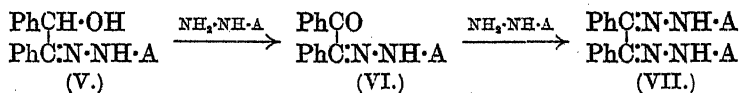
In conformity with the foregoing interpretation, benzoin-δ-benzyl-semicarbazone (1 mol.) and δ-benzylsemicarbazide hydrochloride (2 mols.) reacted in alcoholic solution to give benzildi-δ-benzylsemi-carbazone (1 mol.), which, being practically insoluble, separated almost quantitatively. δ-Phenylsemicarbazide gave similar results.

Biltz's statement " Das Diphenylimidazolon ist andererseits aus Benzoinsemicarbazone unter Austritt der Bestandteile von Hydroxyl-amine entstanden zu denken : $C_{15}H_{15}O_2N_3 = H_3NO + C_{15}H_{12}ON_2$ "

has no experimental foundation whatsoever. To depict such a change would require an unusual interchange of atoms and bonds. Benzoin and δ-benzylsemicarbazide hydrochloride interact to give the mono- and di-δ-benzylsemicarbazones of benzil, but no iminazolone, and hence no benzylhydroxylamine, is formed. This renders untenable Biltz's view that the oxidation of benzoin or benzoinsemicarbazone is occasioned by hydroxylamine.

Whilst benzoin-δ-benzylsemicarbazone is stable in alcohol, an alcoholic solution containing a few drops of hydrochloric acid gave, after some days, benzildi-δ-benzylsemicarbazone. This conversion must be due, in the first instance, to hydrolysis of at least a portion of the benzoin derivative, since otherwise there would be no free hydrazide to combine with the ketonic group formed in the oxidation. This influence of hydrochloric acid is also evinced by the fact that a dilute aqueous-alcoholic solution of benzoin and δ-benzylsemicarbazide hydrochloride gave less benzildi-δ-benzylsemicarbazone and more benzoin-δ-benzylsemicarbazone than did a more concentrated solution of the same reactants. The oxidation of the :CH·OH group would therefore seem to be dependent on the acid in the semicarbazide hydrochloride employed, a conclusion supported by the absence of benzil derivatives when benzoin and semicarbazides (as hydrochlorides) condense in pyridine solution.

The condensation of benzoin with semicarbazides in pyridine solution, in addition to opening up a new method of semicarbazone formation which will be extended, gave excellent yields of the semicarbazones. In three cases, tabulated below, isomerides were obtained.

M. p. of	α-Form.	β-Form.	
Semicarbazone	206°	187°	
δ-Phenylsemicarbazone	198	169	
δ-Benzylsemicarbazone		115°	
δα-Phenylethylsemicarbazone *	174	154	137° (γ-form)

* Unpublished work.

Excepting the last-mentioned instance, the yield of β-isomeride was comparatively small. The benzylsemicarbazone, of which only one form was isolated after recrystallisation from various solvents, would seem from its low melting point to be a mixture. The higher-melting modification of the stereoisomeric semicarbazones is termed the α-isomeride; this is in accordance with the practice adopted by Wilson (J., 1912, 101, 1482; 1913, 103, 377, 1504), Wallach (Ber., 1898, 28, 1955), and Forster (J., 1910, 97, 2156).

According to Biltz (loc. cit.), who evidently carried out the operation in aqueous solution, when benzoinsemicarbazone is heated

with hydrochloric acid, hydrolysis to benzoin and semicarbazide is immediately followed by reduction of the ketone to hydrobenzoin. The author has found, however, that benzoinsemicarbazone (α-form), like all the semicarbazones described in this paper, when heated with alcohol and hydrochloric acid for a short time is quickly hydrolysed, giving benzoin.

E X P E R I M E N T A L.

Benzoinsemicarbazone.—Solutions of 8·5 g. (1 mol.) of recrystallised semicarbazide hydrochloride in 20 c.c. of water and of 16 g. (1 mol.) of benzoin in 160 g. of pyridine were mixed in the cold, kept for 6 days, and poured into 2400 c.c. of cold water. The precipitate, collected after an hour and recrystallised from alcohol, consisted almost entirely of benzoinsemicarbazone (α-form : m. p. 205—206°), previously described by Biltz. The aqueous pyridine filtrate, diluted to 3500 c.c. and left over-night, deposited a second crop which, although much more soluble in alcohol, gave from this solvent, after standing over-night, a proportion of the α-isomeride which was collected. The alcoholic filtrate usually contained a little more of this modification, which was removed by careful treatment involving evaporation, addition of cold alcohol to the mother-liquor in contact with the separated product, and collection of the undissolved portion; this treatment was repeated until small, almost cubical, crystals of the β-*isomeride* appeared and grew as the solution evaporated to small bulk. The final mother-liquor, diluted with water to incipient cloudiness and decolorised with neutral animal charcoal, gave a little more of the β-compound, the whole of which was recrystallised twice from alcohol, giving colourless, almost cubical crystals not changed by further recrystallisation; m. p. 186—187° (decomp.) (Found : N, 15·7 ; M, ebullioscopic in alcohol, 279. $C_{15}H_{15}O_2N_3$ requires N, 15·6% ; M, 269). The β-isomeride, which is moderately soluble in boiling benzene or boiling ether and insoluble in water, differs greatly from the α-modification in solubility and crystalline form. A mixture of both forms melts at 179—200°.

Hydrolysis.—Both forms, when separately dissolved in alcohol and boiled for a minute or two with concentrated hydrochloric acid, gave, on cooling and dilution with water, crystals of benzoin which, after recrystallisation from alcohol, were identified by physical tests and by conversion into benzoin benzoate, m. p. 124° (Wren, J., 1909, 95, 1601, gives m. p. 124—125°). Hydrobenzoin mono- and di-benzoates melt at 160° and 247°, respectively.

Benzildi-δ-benzylsemicarbazone.—This compound was slowly formed in good yield as a crystalline precipitate when solutions

of 4 g. (1 mol.) of δ-benzylsemicarbazide hydrochloride in 8 c.c. of
water and of 4 g. (1 mol.) of benzoin in 75 c.c. of alcohol were mixed
and kept 4—5 days at room temperature.   The action may be
hastened by warming.   When separation of this disemicarbazone
had ceased, the mother-liquor, by evaporation or by dilution with
water, gave three products, viz., a little more benzildi-δ-benzyl-
semicarbazone, some benzilmono-δ-benzylsemicarbazone, and about
1·5 g. of benzoin; the first of these, being almost insoluble in boiling
90% alcohol, and the second, being moderately soluble in the cold,
were easily separated from benzoin by treatment with this solvent.
The final mother-liquor gave a viscous product which did not solidify.
Benzilmono-δ-benzylsemicarbazone, obtained in small quantity as
six-sided plates, m. p. 198°, was hydrolysed to benzil by boiling
alcohol and hydrochloric acid (Found : N, 11·5. $C_{22}H_{19}O_2N_3$
requires N, 11·8%).   The *dibenzylsemicarbazone*, irregular, minute
scales (m. p. 239—240°) from glacial acetic acid–alcohol, was identi-
fied by comparison with an authentic specimen, and by hydrolysis
to benzil by heating for ½ hour with a mixture of glacial acetic and
hydrochloric acids.   It is insoluble in water, ether, or light petroleum,
almost insoluble in alcohol or benzene, and is unchanged by short
boiling with caustic soda or hydrochloric acid (Found :· N, 16·55.
$C_{30}H_{28}O_2N_6$ requires N, 16·7%).

The same compound was formed when 1 g. (1 mol.) of benzoin-δ-
benzylsemicarbazone in 10 c.c. of alcohol was heated at 60° for a
few hours with 1·1 g. (2 mols.) of δ-benzylsemicarbazide hydro-
chloride in 2 c.c. of water, and also when a mixture of benzil (1 g.)
in hot alcohol (10 c.c.) with excess of δ-benzylsemicarbazide hydro-
chloride (5·8 g.) in alcohol (20 c.c.) was heated to boiling for 15
minutes and then at 60° for some hours.   In both cases the product
was collected after 12 hours and purified as above, the yield being
nearly theoretical.

Benzoin-δ-benzylsemicarbazone.—Alcoholic method.—Solutions of
4 g. (1 mol.) of δ-benzylsemicarbazide hydrochloride in 8 c.c. of
water and of 4 g. (1 mol.) of benzoin in 130 c.c. (nearly double the
previous amount) of alcohol were mixed and left for 9 days at the
ordinary temperature until separation of benzildi-δ-benzylsemi-
carbazone had ceased.   Water (40 c.c.), added to the filtrate,
precipitated the remainder of this compound and a little benzoin,
which were collected.   In an hour or so, the filtrate began to deposit
crystals of benzoin-δ-benzylsemicarbazone, the separation of which
was, after some time, rendered complete by the addition of water.
The yield (about 5 g.) of benzoin derivative is attributed to the large
amount of alcohol used.

Pyridine method.—Cold solutions of 5 g. (1. mol) of δ-benzylsemi-

carbazide hydrochloride in 5 c.c. of water and of 5 g. (1 mol.) of benzoin in 50 c.c. of pyridine were mixed and left for 5 days at room temperature. The mixture was then diluted with 100 c.c. of water and poured into 2 litres of well-stirred cold water. The precipitated semicarbazone, when collected and recrystallised twice from alcohol, gave long, fine needles, m. p. 115°, which were unchanged by recrystallisation from other solvents.

Benzoin-δ-benzylsemicarbazone is easily soluble in chloroform or alcohol, less soluble in ether or benzene, and insoluble in light petroleum or water, and in alcoholic solution is hydrolysed by hydrochloric acid to benzoin and δ-benzylsemicarbazide hydrochloride. Yield : 90% (Found : N, 11·5. $C_{22}H_{21}O_2N_3$ requires N, 11·6%).

Benzoin-δ-phenylsemicarbazone.—Alcoholic method : α-Form.— When 4 g. (1 mol.) of δ-phenylsemicarbazide hydrochloride dissolved in 8 c.c. of water were added to a solution at 45° of 4 g. (1 mol.) of benzoin in 130 c.c. of alcohol, and the mixture was kept at room temperature, separation of the *phenylsemicarbazone* (α-form) began after 18 hours and continued for 2 days. Water added to the filtrate precipitated a little more of the product. Recrystallisation from alcohol, in which it was difficultly soluble, gave a woolly mass of fine needles, m. p. 198° (decomp.) (Found : N, 12·2. $C_{21}H_{19}O_2N_3$ requires N, 12·2%). The almost theoretical yield is partly attributed to the sparing solubility of the compound causing separation before oxidation to a benzil derivative can take place. The compound should prove useful for the identification of small quantities of benzoin, into which it is hydrolysed by heating with alcohol and hydrochloric acid.

*Pyridine method : α- and β-Forms.—*When 5 g. of δ-phenylsemicarbazide were added to a cold solution of 6·5 g. of benzoin in 45 c.c. of pyridine, complete solution took place. The mixture, after standing 6 days at room temperature, was diluted with water to incipient cloudiness and kept over-night; the precipitate was collected and the filtrate treated with water as before. Next day, the second crop was collected, and this completed the separation of the α-isomeride, which was purified as previously described. Further addition of water to the pyridine liquor precipitated an emulsion which absorbed much colouring matter from the solution and solidified later as small hard spheres; these were collected, washed, and dried. Decoloration, although difficult, was effected by diluting an ethereal solution with light petroleum to incipient cloudiness and boiling with animal charcoal. The filtrate slowly deposited hard, stout prisms which, when sifted from a little of the α-isomeride and recrystallised from the minimum of alcohol by spontaneous evaporation, gave clusters of needles, m. p. 169°. The

β-*isomeride*, unlike the α-form, is easily soluble in alcohol, moderately soluble in ether or benzene, insoluble in water or petroleum; on heating with alcohol and hydrochloric acid, it yields benzoin; and when mixed with the α-form, it melts at 160–165° (Found : N, 12·3%).

[With MAGNUS HERD.] *Benzildi-δ-phenylsemicarbazone.*—One gram of benzil in 10 c.c. of hot alcohol was heated under reflux with 2·8 g. (excess) of δ-phenylsemicarbazide hydrochloride in a little hot water for 3 hours. After 12 hours, the product was collected and recrystallised twice from glacial acetic acid, separating in rhombic plates, m. p. 253° (decomp.) (70% yield), moderately soluble in alcohol, insoluble in water (Found : N, 17·8. $C_{28}H_{24}O_2N_6$ requires N, 17·6%). The same compound was formed when a mixture of 1 g. (1 mol.) of benzoin-δ-phenylsemicarbazone in 20 c.c. of alcohol with 1·2 g. (2 mols.) of δ-phenylsemicarbazide hydrochloride in a little water was heated under reflux for 2 hours. After concentrating and keeping, the product was purified as before. It was also obtained when a mixture of 2 g. (1 mol.) of benzoin in 20 c.c. of hot alcohol with 5·5 g. (3 mols.) of δ-phenylsemicarbazide hydrochloride in 4 c.c. of water was heated under reflux for 3 hours, the product being worked up as in the last-mentioned instance.

CLXXV.—*The Composition of Starch Iodide.*

By HUMPHREY DESMOND MURRAY.

THE composition of the blue compound produced by the reaction of iodine with starch in the presence of iodides has been the subject of numerous investigations, which have led to somewhat indefinite results (Mylius, *Ber.*, 1887, **20**, 688; Andrews and Goettsch, *J. Amer. Chem. Soc.*, 1902, **24**, 865; Harrison, P., 1910, **26**, 252; Barger and others, J., 1912, **101**, 1394; 1915, **107**, 411; 1924, **125**, 2407). According to Mylius, the blue compound formed in the presence of hydriodic acid has the composition $(C_{24}H_{40}O_{20}I)_4,HI$, and in dilute solution in presence of excess of iodide changes to a purplish-red compound; the ratio of iodine to hydrogen iodide is 4 : 1 for the blue compound and 2 : 1 for the red. Other inves-

tigators, however, have found the iodine content to vary within wide limits and have therefore concluded that an adsorption compound of iodine with starch is formed.

Iodine also forms blue compounds with other organic substances, many of which have been investigated by Barger and his associates. In the case of cholalic acid these workers found, for the mixed crystals formed in the presence of large iodine concentrations, a formula which corresponds more or less with that of Mylius given above, viz., $(C_{24}H_{40}O_5I)_4,KI$.

The object of the present investigation was to determine the composition of the so-called starch iodide by examining the concentrations of free and combined iodine in the resultant solution when iodine dissolved in carbon tetrachloride is shaken with a solution of starch containing a known amount of potassium iodide. In order to calculate the concentration of the tri-iodide ion, the equilibrium concentration of the iodide ion was measured by means of an iodine electrode. Such determinations are most significant in solutions containing small concentrations of potassium iodide, and for precise measurements, therefore, it is necessssary to take into account the hydrolysis of iodine. In order to utilise the results of determinations of this hydrolysis in acid solution (this vol., p. 882), the present measurements were carried out in the presence of acid of the same concentration.

The iodine used was sublimed several times without the addition of potassium iodide. The starch solution was prepared from maize starch. This (10 g.) was shaken with 200 c.c. of $0.0001N$-sulphuric acid, allowed to settle for some hours, washed with water by decantation over a period of 3 days, and dried first at 50° and finally at 110°. A solution of 2·5 g. of the starch powder in 500 c.c. of $N/10$-sulphuric acid was boiled for 1 minute, kept for 12 hours, and decanted from the small cellulose residue. Each series of measurements was made with the same solution, and was completed within 48 hours of the final decantation. Maize starch was chosen for the reason that its solution gives a precipitate less easily than that from potato starch and leaves less residue after boiling than those from the samples of wheat and rice starch obtainable.

When iodine dissolved in dilute potassium iodide solution is added to a solution of starch, a definite threshold concentration of the iodine is necessary before the blue colour appears. This necessitates a correction when dilute iodine solutions, such as were used in the present experiments, are being titrated. Treadwell (" Analytical Chemistry," 4th ed., Vol. II, p. 653) has pointed out that the amount of iodine solution which must be added to a starch solution to produce a blue coloration is directly proportional

to the volume of the starch solution. This result was confirmed, and with concentrations of starch and potassium iodide varying over fairly wide ranges, the iodine threshold concentration was found to have a constant value of 0.15×10^{-5} mol./litre (Meineke, *Chem. Ztg.*, 1894, **18**, 157).

Carbon tetrachloride free from sulphur was dried over calcium chloride and distilled while the temperature was constant. The requisite quantity of iodine was then dissolved in it, and the solution shaken with small quantities of water to remove any iodides which might have been formed. This course was shown to be necessary by preliminary experiments.

The procedure adopted throughout the measurements was as follows : In a thermostat at 25°, 10 c.c. of a solution of iodine in carbon tetrachloride were added to 25 c.c. of acid starch solution (and, in the later experiments, a certain volume of a solution of potassium iodide in $N/10$-sulphuric acid) and a sufficient quantity of $N/10$-sulphuric acid to bring the volume of the aqueous layer to 100 c.c. The whole was then shaken. When equilibrium had been established, 50 c.c. of the aqueous layer were poured into the electrode vessel, and the remainder was titrated against thiosulphate solution, which was repeatedly standardised. The solutions were not exposed to direct sunlight, and it was shown by preliminary experiments that measurable oxidation of very dilute potassium iodide solutions such as were used in the experiments does not take place. The electrodes were of platinum slightly coated with platinum black. The cell set up was :

Pt. I_2|Starch $+$ KI $+$ $N/10$-H_2SO_4|$N/10$-H_2SO_4|Hg_2SO_4. Hg.

The fact that iodine in sufficiently high concentration produces a blue coloration in a starch solution in absence of potassium iodide has been attributed to the formation of iodide ions through reduction of the iodine by the starch. A sufficient concentration of iodide ions to form the blue compound, however, might be produced by hydrolysis of the iodine alone. Measurements made to test this point showed that iodine was reduced to a slight extent by some substance in the starch, and that the reduction was proportional to the quantity of starch present. The concentration of iodide ions produced by reduction $(= B)$ as opposed to the concentration of the latter due to hydrolysis was calculated as follows :

$[I'][I^.]/[I_2] = K_1$; $[I'][I_2]/[I_3'] = K_2$; $B = [I'] + [I_3'] - [I^.]$;

where $[I_2]$ is the concentration of free iodine calculated from the distribution coefficient of iodine between carbon tetrachloride and $N/10$-sulphuric acid, $[I']$ is the concentration of the iodide ion

measured by the iodine electrode, $[I_3']$ is the concentration of the tri-iodide ion calculated from the equilibrium expression, and $[I^·]$ is the concentration of positive iodine ions, the existence of which was assumed in determining the value of K_1.

In Table I is shown the value of B for a starch solution which had been shaken with a solution of iodine in carbon tetrachloride so as to produce the concentration of titratable iodine (A) shown in the first column.

TABLE I.

$A \times 10^4$.	$[I_2] \times 10^4$.	E.	$[I'] \times 10^4$.	$B \times 10^4$.
0·093	0·078	+0·2331	0·028	+0·028
0·257	0·228	+0·1439	0·020	+0·019
0·743	0·647	+0·1816	0·0077	±
2·16	1·96	+0·2285	0·0022	−0·085

Concentrations are given in mols./litre. E is the E.M.F. measured, referred to the mercurous sulphate electrode. $[I']$ is calculated from the equation $\log [I'] = 1/0·05911 . (E_x - E) + \frac{1}{2} \log [I_2]$. The value of E_x ($= - 0·0559$ volt) and of the other constants involved are taken from the paper previously mentioned.

It will be seen that B becomes progressively larger as the concentration of iodine diminishes. By comparison with subsequent measurements, this apparent increase is found to be due, not to increased reduction of the iodine, but to the fact that more iodide ions are combined with the starch in concentrated solutions of iodine than in dilute solutions. By extrapolating A to zero, a value of $0·035 \times 10^{-4}$ is obtained for B, which is taken to be its true concentration.

Several series of measurements were made with carbon tetrachloride solutions containing different quantities of iodine. The four given on page 1292 are the most consistent of some twelve carried out.

C is the concentration of potassium iodide added, increased by $0·35 \times 10^{-5}$, the concentration of iodide ions produced by reduction. D is the concentration of iodide ions combined with the starch, calculated from the equation $D = C + [I^·] - [I'] - [I_3']$. F is the concentration of iodine combined with the starch, calculated from the equation $F = A - [I_2] - [I_3']$.

Two points deserve notice in the above table. The first is the absence of a direct relationship between the iodine taken up by the starch and the concentration either of free iodine (Küster, *Annalen*, 1894, **283**, 360) or of the tri-iodide ion (Lottermoser, *Z. angew. Chem.*, 1924, **37**, 84). This is best seen by comparing the results from different series. The second point is that in dilute iodide solutions the quantity of iodine taken up is approximately double

TABLE II.

Series 1. CCl₄ Sol. = 0·002122M.

$A\times10^5$.	$[I_2]\times10^5$.	$E\times10^2$.	$C\times10^5$.	$[I']\times10^5$.	$[I_5]\times10^6$.	$D\times10^5$.	$F\times10^5$.	Log $[I'][I_2]^2$.	Log F.
2·57	2·28	+14·39	0·35	0·199	0·03	0·16	0·29	$\overline{15}$·015	$\overline{6}$·462
3·02	2·22	+12·53	0·84	0·406	0·06	0·43	0·80	$\overline{15}$·301	$\overline{6}$·903
4·16	2·08	+10·38	1·94	0·908	0·14	1·02	2·07	$\overline{15}$·594	$\overline{5}$·316
6·95	1·74	+ 5·45	8·30	5·67	0·71	2·56	5·14	$\overline{14}$·235	$\overline{5}$·711
12·6	1·05	+ 0·64	40·1	28·6	2·2	11·3	11·3	.$\overline{14}$·499	$\overline{4}$·053
16·5	0·57	− 4·35	199·0	144·0	5·9	54·4	15·3	$\overline{14}$·670	$\overline{4}$·185

Series II.   CCl₄ Sol. = 0·006040M.

7·43	6·47	+18·16	0·35	0·077	0·04	0·35	0·96	$\overline{15}$·508	$\overline{6}$·982
10·34	6·11	+14·63	2·41	0·297	0·13	2·12	4·22	$\overline{14}$·045	$\overline{5}$·625
15·09	5·53	+12·35	5·49	0·687	0·27	4·78	9·53	$\overline{14}$·322	$\overline{5}$·979
18·1	5·16	+10·22	10·63	1·52	0·56	9·05	12·9	$\overline{14}$·607	$\overline{4}$·111
23·0	4·56	+ 7·01	51·8	4·99	1·6	46·7	18·3	$\overline{13}$·016	$\overline{4}$·262
25·5	4·26	+ 5·91	103·2	7·41	2·3	95·6	21·0	$\overline{13}$·129	$\overline{4}$·322
30·2	3·68	+ 2·13	157	30·0	8·0	126	25·7	$\overline{13}$·609	$\overline{4}$·410

Series III.   CCl₄ Sol. = 0·01358M.

16·2	14·6	+22·56	0·35	0·021	0·02	1·01	1·6	$\overline{15}$·651	$\overline{5}$·204
18·3	14·3	+21·02	1·38	0·038	0·04	1·71	4·0	$\overline{15}$·890	$\overline{5}$·602
19·4	14·2	+19·44	2·41	0·070	0·07	2·53	5·2	$\overline{14}$·149	$\overline{5}$·716
24·6	13·6	+17·84	5·49	0·127	0·12	5·45	11·0	$\overline{14}$·371	$\overline{4}$·041
30·3	12·9	+13·39	10·63	0·699	0·65	9·88	17·3	$\overline{13}$·066	$\overline{4}$·238
36·8	12·1	+ 8·44	51·8	4·66	4·0	46·7	24·3	$\overline{13}$·834	$\overline{4}$·386
40·6	11·6	+ 6·44	103·2	9·95	8·3	92·4	28·2	$\overline{12}$·127	$\overline{4}$·450

Series IV.   CCl₄ Sol. = 0·01819M.

21·6	19·6	+22·85	0·35	0·022	0·03	1·20	2·0	$\overline{15}$·927	$\overline{5}$·301
23·9	19·3	+20·79	1·94	0·048	0·07	2·28	4·6	$\overline{14}$·252	$\overline{5}$·663
32·3	18·3	+16·71	8·30	0·228	0·30	8·12	14·0	$\overline{14}$·883	$\overline{4}$·146
40·8	17·2	+ 8·15	19·9	6·23	7·7	12·9	22·8	$\overline{12}$·265	$\overline{4}$·358
77·1	12·8	− 2·43	415	330	304	55	33·9	$\overline{11}$·733	$\overline{4}$·530

that of the combined iodide ion. This suggests the formation of a compound of the form StI_5', where St denotes the starch aggregate involved. To examine this point, log$F$ (as a measure of the concentration of StI_5') has been plotted against log $[I'][I_2]^2$.

It will be seen that in dilute iodide solutions the points from all four series lie on the same straight line, if allowance be made for experimental error, which must necessarily be large in these very dilute solutions. The equation to the straight line is

$$\log\,[I'][I_2]^2 = \log\,F + \overline{10}\cdot42.$$

Hence we obtain the somewhat unexpected result,

$$[I'][I_2]^2/F = 2\cdot6 \times 10^{-10}.$$

This behaviour is not consistent with the formation of an adsorption compound. It could be explained if an I_5' ion were to dis-

tribute itself between the starch phase and the dispersion medium in a constant ratio.   Deviations in the presence of comparatively large concentrations of potassium iodide might be explained by a coagulative effect of the iodide ions.   Amongst other reasons, the lack of evidence for the existence of such an ion makes this explanation improbable.   A more likely explanation is that an addition compound is formed by the starch with one iodide ion and two iodine molecules.   Whilst the starch is in excess, the straight-line relationship found is a close approximation to the truth.   In addition, the subsequent shape of the curve is such as we should expect to find.   On this hypothesis, the point at which the straight-line relationship ceases to be obeyed corresponds to the point at

FIG. 1.
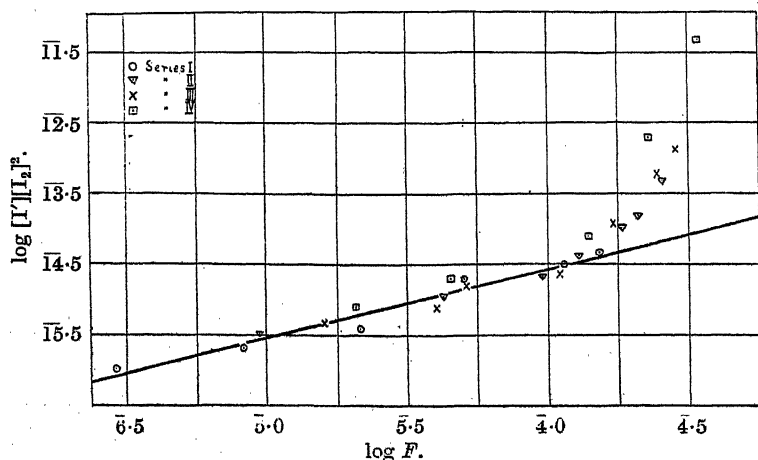
which the concentration of StI_5' becomes comparable with the original concentration of the starch.   We shall not be making an error in orders of magnitude, if we write as an approximation at this point, $[StI_5'] = \frac{1}{10}[St]$ and therefore $[St] = 5F$.   Then, writing for the compound formed $(C_6H_{10}O_5)_nI_5'$ and taking $F = 1 \times 10^{-4}$, and the concentration of the starch as $1 \cdot 25$ g./litre, we obtain $n = 15 \cdot 4$.   The agreement of this value with the analytical results of Mylius and others is probably due to a certain extent to chance.   To obtain complete agreement, it is necessary to assume that the undissociated compound is the hydrogen salt of the above complex anion.   The concentration of the hydrogen ions, however, being in considerable excess of those of the other reacting substances, may be considered constant, and does not appear in the mass action relationships.

In dilute iodide solutions, the formation of a compound anion StI$_5$′ is deduced from the equilibrium expression.   At higher iodide concentrations, it is obvious from the tabulated results that the iodide ion is taken up in excess of the requirements of this compound, pointing possibly to the formation of StI$_3$′, and even of StI′.

Summary.

The concentrations of the various substances formed when a solution of iodine in carbon tetrachloride is shaken with an aqueous solution of starch, with and without the addition of small quantities of potassium iodide, have been measured and the results tabulated. From considerations based upon these results, it is suggested that an addition compound is formed by the starch, the anion of which, in dilute potassium iodide solutions, has the formula $(C_6H_{10}O_5)_nI_5$′, where *n* is approximately 15.

CLXXVI.—*The Formation of* d-2 : 2 : 4-*Trimethylcyclo-hexan*-3-*one*-1-*carboxylic Acid from* d-*Camphorquinone.*

By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

IT has been shown by one of us (J., 1923, **123**, 2648) that when *d*-longifquinone is heated with an acetic acid solution of hydrogen bromide a keto-acid, $C_{15}H_{24}O_3$, results from the addition of water to the diketone and molecular rearrangement.   At the same time, attention was directed to the similarity between this reaction and the action of sulphuric acid on camphorquinone investigated by Manasse and Samuel (*Ber.*, 1897, **30**, 3157; 1902, **35**, 3831) whereby a ketonic acid, $C_{10}H_{16}O_3$, is obtained.   In view of the latter reaction having a possible bearing on the former, and consequently on the constitution of *d*-longifolene, we have considered it desirable to investigate the constitution of the keto-acid obtained by Manasse and Samuel, a problem which those authors made little attempt to solve.

Manasse and Samuel did not determine the optical rotatory power of the acid and of its derivatives which we have found to be of considerable service in elucidating the constitution of the

acid. We have confirmed in all respects the previous work, although we have found it much more difficult to obtain the pure acid than the original description led us to expect.

The constitution of the acid was established in the following manner. On oxidation with nitric acid, the keto-acid was converted into a tribasic acid, $C_9H_{14}O_6$, m. p. 156—157°, which, on distillation, was converted into an anhydride, m. p. 98°. Although direct comparison was not possible, there can be little doubt that this acid is β-methylpentane-βγε-tricarboxylic acid (II), which was prepared synthetically by Perkin and Thorpe (J., 1904, 85, 135). This being the case, the keto-acid, since it is obtained from camphorquinone, may be best represented by formula (I), that is, *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid.*

(I.) $\begin{array}{l} CH_2-CHMe\!-\!-\!-\!CO \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$ $\begin{array}{l} CH_2\cdot CO_2H \\ CH_2\cdot CH(CO_2H)\cdot CMe_2\cdot CO_2H \end{array}$ (II.)

(III.) $\begin{array}{l} CH_2\cdot CHMe\!-\!-\!-\!CH\cdot OH \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$ $\begin{array}{l} CH_2\!-\!CMe\!=\!=\!CH \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$ (IV.)
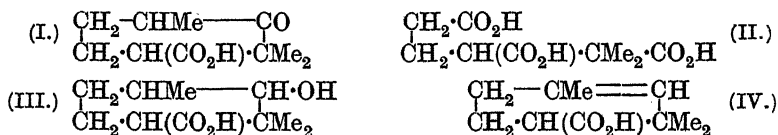
It was shown by Manasse and Samuel that when the keto-acid was reduced with sodium amalgam it yielded a hydroxy-acid which showed no tendency to form a lactone; since this acid can only be represented by formula (III) (3-hydroxy-2 : 2 : 4-trimethyl*cyclo*hexane-1-carboxylic acid) it must be the *trans*-form of the acid. When the *methyl* ester of the hydroxy-acid was treated with phosphorus pentachloride, a mixture of a chloro-ester and unsaturated ester was obtained from which, after treatment with diethylaniline, the pure unsaturated ester was separated. Although the quantity available was insufficient for detailed investigation, there can be little doubt that it was *methyl* 1-2 : 2 : 4-*trimethyl-*Δ³-*cyclohexene-1-carboxylate* (IV), the acid obtained on hydrolysis being an oil which was lævorotatory in ethyl-alcoholic solution.

Since the keto-acid tended to separate as an oil which crystallised very slowly, we attempted to utilise the crystalline methyl ester for its purification. This ester, in accordance with the statement of Manasse and Samuel, was readily obtained crystalline, but was always obtained mixed with a liquid ester. The mixture distilled as a homogeneous substance, and after the solid had been separated by filtration the liquid portion, possessing the same molecular composition as the solid, could not be induced to crystallise. It therefore appeared possible that this liquid form of the ester con-

* It is conceivable that the hydrolysis may pursue an alternative course which would lead to an acid of the constitution $\begin{array}{l} CH_2\cdot CO\!-\!-\!-\!-\!CHMe \\ CH_2\cdot CH(CO_2H)\cdot CMe_2 \end{array}$. This acid and (I) would both give (II) on oxidation.

sisted of an equilibrium mixture of the keto- and enol forms, although it gave no colour with ferric chloride. This view has received support from a careful investigation of the semicarbazones of the ester. The pure crystalline ester on treatment with semicarbazide under suitable conditions (see p. 1300) yielded a mixture of α- and β-semicarbazones. Both these semicarbazones gave on hydrolysis an ester which only partly crystallised, the quantity of crystalline ester obtained from each of them being approximately the same. A mixture of the same two α- and β-semicarbazones was also obtained from the liquid ester and there would therefore appear to be little doubt that the liquid ester is a mixture of the keto- and enol forms. It was, in fact, found possible, starting from 100 grams of the crude acid, to convert all except about 10 grams into the crystalline ester by means of the semicarbazones.

When the pure crystalline methyl ester was hydrolysed with alcoholic potassium hydroxide solution in the usual manner, the acid obtained on acidification still tended to separate as an oil and, although eventually crystallising as a hard cake, it had not the appearance of a homogeneous substance. A quantity of the acid was therefore crystallised from water and separated into two main fractions which melted respectively at 71—72° and 65—69°. When examined polarimetrically in alcoholic solution, the two fractions showed a marked difference in rotatory power, the specific rotation of the first fraction being very much higher than that of the second. When dissolved in sodium hydroxide, the specific rotation of the first fraction was again higher than that of the second fraction and mutarotation from a higher to a lower value was also observed, the relative change in rotatory power being practically the same in both cases. These observations explained at once the great difficulty experienced in purifying the acid even when prepared from the pure ester, since it was clear that the acid undergoes racemisation in alkaline solution. This is accounted for by the fact that a change from the enol to the keto-form involves one of the asymmetric carbon atoms and although in this reversible change complete racemisation is unlikely owing to the presence of the second asymmetric carbon atom in the molecule, yet partial racemisation is sure to take place.*

* Another explanation of the above phenomena which may not involve a keto ⇌ enol change in the case of γ- or δ-keto-acids and esters is the following : the keto-acid and ester possess two centres of asymmetry, $-CH_2-*CHMe-CO-$ and $-CH_2-*CH(CO_2H)-CMe_2-$, which may be distinguished as X and Y respectively. X may easily suffer racemisation and Y would be more difficult to racemise. On this view, the crystalline ester would be " + X + Y " and the liquid ester an equilibrium mixture " + X + Y ⇌ X + Y."

Reference has been made above to the fact that the methyl ester gave rise to two semicarbazones. When the preparation was carried out using sodium acetate to liberate the semicarbazide, the yield of the β-semicarbazone was very small, whilst if sodium bicarbonate or potassium carbonate was used the β-form was the main product of the reaction. This indicated that the β-form is unstable and tends to pass into the α-form in the presence of acetic acid. This has been confirmed by polarimetric observations. A solution of the α-form in acetic acid showed a small but definite mutarotation from a higher to a constant lower value; a mixture of the α- and β-forms showed a much more marked mutarotation, whilst the α-form showed a considerable mutarotation from a lower to a constant higher value, the final value being the same in all three cases.

That the mutarotation was due to the acetic acid was proved by the fact that the β-semicarbazone showed no mutarotation when dissolved in alcohol (owing to its sparing solubility the α-semicarbazone could not be examined in this solvent), but on the addition of a small quantity of acetic acid mutarotation was observed. The semicarbazones have optical rotatory powers of opposite sign to those of the corresponding acid and methyl ester.

A somewhat analogous case of the conversion of a *syn*- into an *anti*-form (or *vice versa*) accompanied by mutarotation was observed by Forster (J., 1905, **87**, 237), who showed that of the three oximes formed from *iso*nitrosocamphor on treatment with magnesium methyl iodide, the α-oxime passed into the γ-oxime when exposed to light in chloroform solution, the change being accompanied by a diminution in the specific rotation. By removal of the solvent Forster recovered the whole of the α-oxime in the form of the γ-oxime. In the case of the semicarbazones, we have not been equally successful owing to the difficulty of removing the acetic acid, but we have established the fact that from all the solutions only the stable α-form could be separated. In our opinion there can be no doubt that the mutarotation is caused by the change of the unstable β-form to the stable α-form, the final observed rotation being that of the equilibrium mixture of the two. Apart from the above, it should be noted that the rotatory power of the pure α-semicarbazone in acetic acid solution falls from a higher to a lower value; that of the pure β-semicarbazone rises from a low value to a higher value and then falls again to the constant value, higher than that observed at first; whilst mixtures of the two show rotatory powers which at the beginning are higher than any recorded in the cases of the pure semicarbazones and which fall to the lower constant values. It would appear that this case of

mutarotation is worthy of detailed investigation. Tentatively, we suggest that the results obtained point to the formation of an intermediate compound (? salt formation) of high rotatory power in the conversion of the β- into the α-form and that this has not been observed in the conversion of the α- into the β-form.

It is hoped by extending this work to the investigation of substituted camphorquinones to throw some light on the question of the constitution of the β-derivatives of camphor.

EXPERIMENTAL.

d-2 : 2 : 4-*Trimethylcyclohexan-3-one-1-carboxylic acid* (I), prepared by Manasse and Samuel's method (*loc. cit.*), was obtained as an oil which only partly crystallised. It was purified most conveniently by conversion into the methyl ester by treatment with methyl alcohol and sulphuric acid, when, on extraction with ether and removal of the solvent, the ester was obtained as an oil which rapidly partly crystallised in long needles. The solid ester was separated and the oil, which as a rule formed 60% of the total yield, was reserved for later investigation (see below).

Methyl d-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylate crystallised from dilute methyl alcohol in fine, long needles which melted, as stated by Manasse and Samuel, at 82—83°. The ester was readily volatile in steam, and sublimed in a vacuum at the ordinary temperature (Found : C, 66·6; H, 9·0. Calc., C, 66·6; H, 9·1%).

The rotatory power was determined at 15° in ethyl-alcoholic solution; $c = 0.9908$, $l = 4$, $\alpha_{5461} = + 2.55°$, $[\alpha]_{5461} = + 64.33°$.

After hydrolysis of the ester with alcoholic potassium hydroxide solution, the acid separated on acidification of the aqueous alkaline solution as a viscid oil which slowly crystallised when kept at 0°. The acid crystallised from water in needles, m. p. 71—72°. On allowing the mother-liquor to evaporate slowly in a vacuum desiccator over sulphuric acid, crystals and some oil slowly separated. The material was collected and again crystallised from water with the same result. The crystalline solid melted at 67—69°, softening somewhat at 60°. As has already been mentioned, the explanation of this apparent non-homogeneity of the acid prepared from the pure crystalline ester was explained by partial racemisation accompanied by enol-keto change.

In ethyl-alcoholic solution at 15°, the acid shows no mutarotation : first fraction, $c = 1.0346$, $l = 4$, $\alpha_{5461} = + 1.96°$, $[\alpha]_{5461} = + 47.4°$; second fraction, $c = 0.9626$, $l = 4$, $\alpha_{5461} = + 0.72°$, $[\alpha]_{5461} = + 18.7°$.

A solution of the acid in a very slight excess of the calculated

quantity of aqueous sodium hydroxide displayed definite muta-rotation at 15°; the rotatory power was constant after 48 hours : first fraction, $c = 0.9784$, $l = 4$, $\alpha_{5461} = + 0.87°$, $[\alpha]_{5461} = + 22.2°$, changing to the constant values $\alpha_{5461} = + 0.59°$ and $[\alpha]_{5461} = + 15.1°$; second fraction, $c = 1.0226$, $l = 4$, $\alpha_{5461} = + 0.33°$, $[\alpha]_{5461} = + 8.1°$, the final values being $\alpha_{5461} = + 0.21°$ and $[\alpha]_{5461} = + 5.1°$.

The semicarbazone, prepared in the usual manner, was obtained as a very sparingly soluble crystalline powder which, after crystal-lisation from a large volume of alcohol, decomposed at 228—229°, a somewhat higher melting point than that observed by Manasse and Samuel (Found : C, 54.9; H, 7.7. Calc., C, 54.8; H, 7.9%).

The α-oxime, prepared in alkaline solution as described by Manasse and Samuel, melted at 164—165°; if, however, the oxime was prepared in alcoholic solution, sodium acetate being used to decompose the hydroxylamine hydrochloride, a β-*oxime* was obtained which differed from the α-oxime in being much more sparingly soluble in alcohol, from which it crystallised in thin plates decomposing at 226° (Found: N, 7.2. $C_{10}H_{17}O_3N$ requires N, 7.0%).

The filtrate from which the crystalline ester had been separated was distilled under diminished pressure, when practically the whole distilled as a colourless, viscid oil at 146—155°/20 mm. On keep-ing in the ice-chest for some days, the oil partly solidified; the crystals, which consisted of the ester, m. p. 83°, were collected and the oil was redistilled, when it boiled at 135—140°/10 mm. Analysis showed this to be the pure methyl ester and, as has been suggested above, it was in all probability an equilibrium mixture of the keto- and enol forms. In alcoholic solution, it gave no colour with ferric chloride (Found : C, 66.2; H, 9.4. $C_{11}H_{18}O_3$ requires C, 66.6; H, 9.1%).

The *oxime*, prepared by treating either the crystalline or the liquid ester with hydroxylamine hydrochloride in alcoholic solution in the presence of sodium acetate, was obtained on removal of the solvent as a semi-solid oil and evidently consisted of a mixture of the *syn*- and *anti*-forms. The crude oxime was drained on porous porcelain until free from adhering oil and crystallised from dilute methyl alcohol, from which it was obtained in colourless needles, m. p. 110—111° (Found : C, 62.0; H, 9.1. $C_{11}H_{19}O_3N$ requires C, 62.0; H, 8.9%).

The oxime did not undergo the Beckmann rearrangement when treated with pyridine and benzenesulphonyl chloride and was recovered unchanged after treatment with these reagents.

The α- and β-Semicarbazones of Methyl d-2 : 2 : 4-*Trimethyl*cyclo-
hexan-3-*one*-1-*carboxylate.*

(i) The *α-semicarbazone* was most readily prepared in a pure state on treatment of the methyl ester (either solid or liquid) in alcoholic solution with an aqueous solution of semicarbazide acetate. The *semicarbazone,* which separated as a thick, white precipitate (yield about 70%), crystallised from much alcohol in glistening leaflets which sintered at 229—230° and decomposed at 231° (Found : C, 56·4; H, 8·1. $C_{12}H_{21}O_3N_3$ requires C, 56·5; H, 8·2%).

The optical rotatory power was determined at 15° in acetic acid solution, definite, but small, mutarotation being observed : $c = 0·9540$, $l = 4$, $\alpha_{5461} = -2·13°$, $[\alpha]_{5461} = -55·8°$; the final values, after 48 hours, being $\alpha_{5461} = -1·91°$, $[\alpha]_{5461} = -50·5°$.

When the mother-liquor of the α-semicarbazone was diluted with water and allowed to remain for several days in the ice-chest, a small quantity of the impure β-semicarbazone, fine needles, m. p. about 150°, was deposited.

(ii) β-*Semicarbazone.*—The methyl ester dissolved in alcohol was mixed with a slight excess of an aqueous solution of semicarbazide hydrochloride to which sufficient sodium bicarbonate had been added to neutralize the hydrochloric acid. On standing for some days with occasional agitation, the semicarbazone separated as a white, crystalline precipitate, which was washed with a little ether and dried on porous porcelain (yield 11 g. from 10 g. of ester). This crude semicarbazone, m. p. about 180°, the rotation of which could not be determined accurately, was dissolved in the minimum of hot alcohol and allowed to crystallise, when colourless leaflets were obtained which softened at 210° and decomposed at 215—216° (A) (yield 3·1g.) (Found : C, 56·8; H, 8·3%).

In acetic acid solution at 15°, mutarotation in the same direction from a high value to the same constant value, reached after 48 hours, was observed : $c = 1·0140$, $l = 4$, $\alpha_{5461} = -2·89°$, $[\alpha]_{5461} = -71·25°$; the final values being $\alpha_{5461} = -2·05°$, $[\alpha]_{5461} = -50·5°$.

Fraction (A), recrystallised from alcohol, gave nearly pure α-semicarbazone, decomp. 221—222°. The optical activity was observed under the same conditions as before, but the constant value was not reached after 40 hours : $c = 1·0686$, $l = 4$, $\alpha_{5461} = -2·90°$, $[\alpha]_{5461} = -67·8°$: after 40 hours the values observed were $\alpha_{5461} = -2·23°$, $[\alpha]_{5461} = -52·2°$.

The original mother-liquor from which fraction (A) had been separated was concentrated to a small bulk under diminished

pressure,* when, on cooling, a large fraction crystallised in soft needles which softened at 158° and melted at 161°. The β-*semi-carbazone*, which was very readily soluble in alcohol, crystallised from dilute methyl alcohol in fine needles, m. p. 161—162° (Found : C, 56·4; H, 7·9%). In acetic acid solution at 15°, the β-semicarbazone shows a mutarotation which rises and falls again to the same constant value, after about 60 hours, as was observed in the other cases. The various observed rotations are quoted : $c =$ 1·0464, $l = 4$, $\alpha_{5461} = -1\cdot60°$, $-1\cdot78°$, $-2\cdot24°$, $-2\cdot19°$, $-2\cdot10°$; $[\alpha]_{5461} = -38\cdot2°$, $-42\cdot5°$, $-53\cdot5°$, $-52\cdot3°$, $-50\cdot2°$.

In ethyl alcohol at the same temperature, no mutarotation was observed during 24 hours : $c = 0\cdot9896$, $l = 4$, $\alpha_{5461} = -0\cdot73°$.

When the solution (volume 49·25 c.c.) was poured out of the tube and mixed thoroughly with acetic acid (0·75 c.c.), marked mutarotation was observed, the following being the various rotations noted during 72 hours : $-0\cdot80°$, $-0\cdot85°$, $-0\cdot99°$, $-1\cdot13°$, $-1\cdot26°$.

Hydrolysis of the α- and β-Semicarbazones.—Both the α- and the β-semicarbazone yielded a mixture of a crystalline and a solid methyl ester on hydrolysis.

(i) The α-semicarbazone (9 g.) was heated on the water-bath with sulphuric acid (5% ; 25 c.c.) until a clear solution was obtained, the ester was taken up with ether, the ethereal extract washed with sodium carbonate solution, dried, and the solvent removed, when a semi-crystalline oil (7 g.) remained which on filtration yielded 4·6 g. of the crystalline ester.

(ii) The β-semicarbazone (6·8 g.), when hydrolysed under similar conditions, yielded the mixed ester (5 g.), from which 2·1 g. of crystalline ester were separated.

Oxidation of d-2 : 2 : 4-*Trimethylcyclohexan-3-one-1-carboxylic Acid with Nitric Acid.* β-*Methylpentane-βγε-tricarboxylic Acid* (II).

A mixture of the keto-acid (10 g.) with nitric acid (d 1·27; 250 c.c.) was heated on the water-bath for 3 hours and finally on the sand-bath for 3 hours to complete the reaction. The excess of mineral acid was removed under diminished pressure and finally in a vacuum desiccator over sodium hydroxide, when a viscid oil remained which slowly crystallised. It was best purified by conversion into the triethyl ester, which distilled almost completely at 185—190°/20 mm. The pure ester was hydrolysed with hydrochloric acid, and the crystalline residue which remained after the

* Owing to the distinct volatility of the β-semicarbazone, loss of material could not be avoided during its preparation.

removal of the excess of mineral acid was recrystallised from hydrochloric acid. It melted at 155—157° with loss of water, the m. p. being dependent on the rate of heating. The identity of the acid with that prepared synthetically by Perkin and Thorpe (*loc. cit.*) was confirmed by analysis (Found : C, 69·4; H, 6·3; M, 218·4. Calc., C, 69·5; H, 6·4%; M, 218) and by conversion, on distillation under diminished pressure, into the anhydride, a viscid oil which gradually crystallised in stellate groups of needles and separated from benzene in plates, m. p. 98° * (Found : C, 53·9; H, 5·9. Calc., C, 54·0; H, 6·0%).

trans-d-3-*Hydroxy*-2 : 2 : 4-*trimethylcyclohexane*-1-*carboxylic   Acid* (III) *and* 1-2 : 2 : 4-*Trimethyl*-Δ^3-*cyclohexene*-1-*carboxylic Acid* (IV).

The *trans*-hydroxy-acid was readily obtained from the keto-acid by Manasse and Samuel's method (*loc. cit.*). In solution in ethyl alcohol at 15°, it was of the same sign as the keto-acid; no mutarotation was observed : $c = 1·0146$, $l = 4$, $\alpha_{5461} = + 1·77°$, $[\alpha]_{5461} = + 43·6°$.

The *methyl* ester was a somewhat viscid, colourless oil, b. p. 150—152°/12 mm. (Found : C, 66·2; H, 9·4. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%).

For the preparation of the unsaturated ester, a solution of the hydroxy-ester (18 g.) in ether (100 c.c.) was cooled with ice and gradually treated with finely-divided phosphorus pentachloride (20 g.), which dissolved readily; the reaction was completed by gentle warming. After the addition of ice the ethereal solution was thoroughly washed with sodium carbonate solution (A), dried, and evaporated. The residual oil was distilled, when the bulk of the oil passed over at 120—140°/20 mm. The mixture of chloro- and unsaturated esters was boiled with an excess of diethylaniline for some hours. The ester, which was separated in the usual manner, was fractionated under diminished pressure, when a large fraction was obtained, b. p. 105—107°/14 mm. (Found : C, 72·4; H, 9·8. $C_{11}H_{18}O_2$ requires C, 72·4; H, 10·0%).

Methyl 1-2 : 2 : 4-*trimethyl*-Δ^3-*cyclohexene*-1-*carboxylate*, a colourless, fragrant-smelling oil, gave, when hydrolysed with alcoholic potassium hydroxide solution in the usual manner, the *acid* as a very viscid oil, b. p. 150—152°/16 mm. (Found : C, 70·7; H, 8·7. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%). The acid did not give any indication of mutarotation in ethyl-alcoholic solution during

* In Richter's "Lexikon," Vol. I., p. 1134, the m. p. of the anhydride is wrongly given as 155—157°, which is the m. p. of the acid. The b. p. is also wrongly stated to be 255° instead of 255°/45 mm.

24 hours. Its optical rotatory power is opposite to that of the keto- and of the hydroxy-acid : $c = 2\cdot653$, $l = 4$, $\alpha_{5461} = -4\cdot08°$, $[\alpha]_{5461} = -38\cdot5°$.

1-2 : 2 : 4-*Trimethyl*-Δ^3-*cyclohexene-1-carboxylic acid* could not be induced to crystallise even when kept for several weeks in the ice-chest; in sodium carbonate solution it immediately decolorised a solution of potassium permanganate, whilst in chloroform solution bromine was rapidly absorbed, but the bromo-acid formed decomposed with evolution of hydrogen bromide. The *ammonium* salt, which was somewhat sparingly soluble in water, crystallised in irregular plates, decomp. 147—148°. The *calcium, barium,* and *silver* salts were all sparingly soluble in water; the silver salt was analysed (Found : Ag, 39·3. $C_{10}H_{15}O_2Ag$ requires Ag, 39·3%).

The sodium carbonate solution (A) (see above) was acidified, when a viscid oil separated; this was taken up with ether, the ether dried, and evaporated. The residual oil (5 g.) was triturated with dilute ammonia, when a small quantity of an insoluble oil remained which partially crystallised. The solid was collected, drained on porous porcelain, and recrystallised from dilute methyl alcohol. It was identified as methyl d-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylate, m. p. 82—83°, mixed m. p. 82—83° (Found : C, 67·0; H, 9·1. Calc., C, 66·6; H, 9·1%). The separation of the keto-ester from a sodium carbonate solution is somewhat remarkable, since experiment has shown the crystalline ester to be quite insoluble in cold alkali. It is possible that it dissolved in its enolic form, and this point will be further investigated.* The oil which dissolved in the ammonia was found to consist of the *cyclo*hexene acid.

* It is very improbable that the presence of the keto-ester in the sodium carbonate solution was due to any defect in manipulation, since the same result was obtained in two distinct experiments.

CLXXVII.—*The Action of Halogens on Phenyl-hydrazones. Part II. The Action of Chlorine.*

By JAMES ERNEST HUMPHRIES, HENRY HUMBLE, and ROY EVANS.

THE action of chlorine on phenylhydrazones in cold carbon tetra-chloride solution differs from that of bromine (Humphries, Bloom, and Evans, J., 1923, 123, 1766) in that, whilst bromine enters the benzene nucleus atom by atom, first in the para-position and then in the ortho-position to the group $RR'C:N\cdot NH\cdot$, chlorination leads directly to the 2 : 4-dichloro-derivative $RR'C:N\cdot NH\cdot C_6H_3Cl_2$, even when the phenylhydrazone is present in large excess. More-over, bromination ceases when the dibromophenylhydrazone has been formed, but chlorination proceeds, although with difficulty, a stage farther with formation of the 2 : 4 : 6-trichlorophenyl-hydrazone.

Benzaldehydephenylhydrazone is converted by the action of an excess of chlorine into a *tetrachloro*-derivative,
$$C_6H_5\cdot CCl:N\cdot NH\cdot C_6H_2Cl_3,$$
which is also formed, quantitatively, by the interaction of chlorine (1 mol.) and benzaldehyde-2 : 4 : 6-trichlorophenylhydrazone. This type of substitution occurs, as in the case of the bromination of benzaldehydephenylhydrazone, after chlorine has entered the ortho- and para-positions, the compound $C_6H_5\cdot CCl:N\cdot NH\cdot C_6H_3Cl_2$ (2 : 4) being formed readily from the phenylhydrazone, *p*-chlorophenyl-hydrazone, and 2 : 4-dichlorophenylhydrazone of benzaldehyde. The trichloro-compound cannot be converted into the tetrachloro-compound by the action of chlorine alone. The presence of hydrogen chloride is necessary to produce the change; for example, the con-version is readily effected at 0° in the presence of phenol.
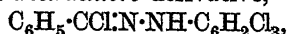
The primary product of chlorination of a phenylhydrazone is a yel-low or orange, usually unstable, precipitate similar to those obtained in the bromination experiments; it consists of the hydrochloride of the chlorophenylhydrazone or of a mixture of the hydrochlorides of the chlorophenylhydrazone and the original phenylhydrazone, according to the proportion of chlorine employed in the experiment.

The stability of a hydrazone towards hydrolysis by an acid depends not only on the nature of the aldehydic or ketonic con-stituent (*loc. cit.*, p. 1767), but also on the strength of the basic one, in which respect phenylhydrazine < *p*-bromophenylhydrazine < 2 : 4-dibromophenylhydrazine, for when, *e.g.*, benzaldehyde-*p*-bromophenylhydrazone is brominated the final product contains *p*-bromophenylhydrazine hydrobromide and benzaldehyde-2 : 4-dibromophenylhydrazone. A corresponding relationship in the case

of the Schiff's bases is evident from the work of Franzen and Henglein (*J. pr. Chem.*, 1915, **91**, 245), for whilst the dibromides of benzylidene-aniline and benzylidene-*p*-bromoaniline gave the hydrobromides of benzylidene-*p*-bromoaniline and benzylidene-2 : 4-dibromoaniline respectively on boiling with alcohol, the dibromide of benzylidene-2 : 4-dibromoaniline decomposed immediately under the same treatment, yielding only 2 : 4 : 6-tribromoaniline. Here again the stability varies with the strength of the basic constituent, in which respect aniline >*p*-bromoaniline >2 : 4-dibromoaniline.

<center>E X P E R I M E N T A L.</center>

Preparation of the Chlorophenylhydrazines.—Reduction with stannous chloride of the diazonium salts obtained from *p*-chloro-, 2 : 4-dichloro-, and 2 : 4 : 6-trichloro-aniline having given very poor yields of the corresponding hydrazines, Davies's method (reduction with ammonium sulphite; J., 1922, **121**, 719) was employed. Since little or no ammonium phenylhydrazinedisulphonate separated from the reaction mixture, this was heated at 80° with concentrated hydrochloric acid, when the hydrochloride of the base separated. *p*-Chloro- and 2 : 4-dichloro-phenylhydrazine were thus obtained in yields of 95%. The yield of 2 : 4 : 6-trichlorophenylhydrazine was only 25%, owing to the simultaneous formation of a brown oil, which solidified on cooling and from which white needles, m. p. 64°, of 1 : 3 : 5-trichlorobenzene were obtained in considerable quantity (Found : Cl, 58·9. Calc., Cl, 58·7%).

<center>*Chlorination of Phenylhydrazones.*</center>

Chlorination was effected by mixing well-cooled solutions (−5° to −10°) of chlorine (1 mol., unless stated otherwise) and the phenyl-hydrazone (1 mol.) in carbon tetrachloride. Usually the temperature rose slightly and an unstable, tarry precipitate formed. This, the primary product, was dissolved in alcohol; the final products were obtained from the alcoholic solution.

The identity of the final products was established by analysis and, in the case of phenylhydrazones, by comparison with synthetically prepared specimens, or in the case of phenylhydrazines, by condensation with benzophenone or benzaldehyde and comparison of the product with the corresponding phenylhydrazone.

Acetonephenylhydrazone.—The pale yellow, crystalline, primary product, which became almost colourless when washed with ether, was dried in a vacuum [Found : Cl (as hydrochloride), 16·4; Cl (total), 32·9%]. These results are very close to those required for the hydrochloride of acetonemonochlorophenylhydrazone (16·2 and 32·4 respectively). Addition of ether to the cold alcoholic

<center>Y Y 2</center>

solution of the primary product gave a precipitate only if the alcoholic solution had been previously boiled. This precipitate was probably a mixture of the hydrochlorides of phenylhydrazine and 2 : 4-dichlorophenylhydrazine, for a determination of the equivalent weight of the base in it gave the value required for monochlorophenylhydrazine, and combination with benzophenone produced a mixture from which a considerable quantity of benzophenonephenylhydrazone was obtained (no other pure hydrazone was isolated).

Acetophenonephenylhydrazone.—A solution in cold alcohol of the yellow primary product deposited crystals of phenylhydrazine hydrochloride, and from the mother-liquor were obtained yellow needles, m. p. 85°, of *acetophenone-2 : 4-dichlorophenylhydrazone* (Found : Cl, 25·95. $C_{14}H_{12}N_2Cl_2$ requires Cl, 25·45%).

Benzophenonephenylhydrazone.—From the yellow alcoholic solution of the primary product (even if excess of hydrazone had been used) was obtained a mixture of the original phenylhydrazone and pale-yellow needles (m. p. 105°) of *benzophenone-2 : 4-dichlorophenyl-hydrazone* (Found : Cl, 20·3. $C_{19}H_{14}N_2Cl_2$ requires Cl, 20·8%).

Benzophenone-2 : 4-dichlorophenylhydrazone.—No substitution took place at 0°. If the hydrazone and halogen were left in contact for 24 hours at the laboratory temperature about one-half of the hydrazone was converted into the 2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 106° (Found : Cl, 28·3. $C_{19}H_{13}N_2Cl_3$ requires Cl, 28·4%).

Benzaldehydephenylhydrazone.—The final product of chlorination with 1 mol. of chlorine was a mixture of benzaldehydechlorophenyl-hydrazones which could not be separated from one another; with 3 mols. of chlorine, the compound $C_6H_5 \cdot CCl:N \cdot NH \cdot C_6H_3Cl_2$ (2 : 4) was obtained; and with excess of chlorine, a tetrachloro-derivative, $C_6H_5 \cdot CCl:N \cdot NH \cdot C_6H_2Cl_3$ (2 : 4 : 6).

Benzaldehyde-p-chlorophenylhydrazone.—The final product was a mixture of the original phenylhydrazone and the compound $C_6H_5 \cdot CCl:N \cdot NH \cdot C_6H_3Cl_2$ (2 : 4), m. p. 90° (Found : Cl, 35·6. $C_{13}H_9N_2Cl_3$ requires Cl, 35·6%).

Benzaldehyde-2 : 4-dichlorophenylhydrazone.—The yellow primary product, while still in suspension in carbon tetrachloride, was treated with a little alcohol, part of the former solvent was removed by distillation, and more alcohol added, when the preceding trichloro-compound rapidly crystallised in needles (yield quantitative). Its properties are very similar to those of the corresponding bromine compound (*loc. cit.*, p. 1771). Reduction in boiling alcoholic solution with zinc dust (6 hours), followed by concentration of the solution and addition of ether and hydrogen chloride, gave 2 : 4-dichlorophenylhydrazine hydrochloride in good yield, and from

this hydrazine were prepared m-*chlorobenzaldehyde*-2 : 4-*dichloro-phenylhydrazone*, yellow prisms, m. p. 127° (Found : Cl, 35·6. $C_{13}H_9N_2Cl_3$ requires Cl, 35·6%), and p-*chlorobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, white needles, m. p. 117° (Found : Cl, 35·7%). The properties of these hydrazones confirm the above formula of the trichloro-compound (compare note below).

Benzaldehyde-2 : 4 : 6-*trichlorophenylhydrazone.*—This experiment, carried out like the preceding one, gave the *tetrachloro*-compound, $C_6H_5\cdot CCl\colon N\cdot NH\cdot C_6H_2Cl_3$ (2 : 4 : 6), yellow needles, m. p. 98°, in quantitative yield (Found : C, 46·3 ; H, 2·4 ; Cl, 42·3 ; *M*, in freezing benzene, 347. $C_{13}H_8N_2Cl_4$ requires C, 46·7 ; H, 2·4 ; Cl, 42·5% ; *M*, 344).

The product was reduced with zinc dust in boiling alcohol (1—2 hours), and 2 : 4 : 6-trichlorophenylhydrazine hydrochloride ultimately obtained (Found : Cl, 57·6 ; equiv., 213.

$$C_6H_2Cl_3\cdot NH\cdot NH_2,HCl$$

requires Cl, 57·25% ; equiv., 211·5). This is probably the best method of preparing 2 : 4 : 6-trichlorophenylhydrazine.

Benzaldehydephenylhydrazone is not reduced by zinc dust in alcoholic solution as are the above chloro-derivatives, which have the hydrogen of the original aldehyde group replaced by halogen.

NOTE.—The compound (white, silky needles, m. p. 114°) to which Humphries, Bloom, and Evans (*loc. cit.*, p. 1771) assigned the formula $C_6H_5\cdot CBr\colon N\cdot NH\cdot C_6H_3Br_2$ was stated by Ciusa and Vecchiotti (*Gazzetta*, 1916, **46**, i, 240) to be p-bromobenzaldehyde-2 : 4-dibromo-phenylhydrazone. We have prepared the latter compound; it is orange-yellow and melts at 128° (Found : Br, 55·2. $C_{13}H_9N_2Br_3$ requires Br, 55·4%).

CLXXVIII.—*The Action of Azides on Toluquinone.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

THE action of azides on quinones was first studied by Wolff and various collaborators (*Annalen*, 1912, **394**, 70 ; 1913, **399**, 274).

From phenyl azide and benzoquinone Wolff obtained four products besides quinhydrone, *viz.*, a triazole, phenylazimino-

quinone (I); two bisaziminoquinones (II and III); and a compound, which formed the bulk of the product, of the composition

$$
\begin{array}{ccc}
\text{CO} & \text{CO} & \text{CO NPh} \\
\text{HC} \quad \text{C---N} & \text{N---C} \quad \text{C---N} & \text{N---C} \quad \text{C} \quad \text{N} \\
\text{HC} \quad \text{C} \quad \text{N} & \text{N} \quad \text{C} \quad \text{C} \quad \text{N} & \text{N} \quad \text{C} \quad \text{C---N} \\
\text{CO NPh} & \text{PhN} \quad \text{CO NPh} & \text{PhN} \quad \text{CO} \\
\text{(I.)} & \text{(II.)} & \text{(III.)}
\end{array}
$$
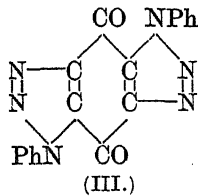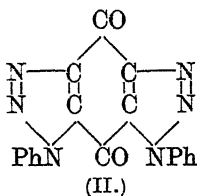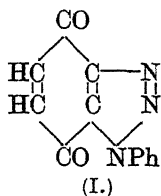
$C_{18}H_{14}O_2N_4$, for which he later suggested the constitution (IV) from analogy with the constitution he assigned to a corresponding derivative obtained from naphthaquinone. He found that this compound on heating lost nitrogen and yielded a compound of the composition $C_{18}H_{14}O_2N_2$ which he assumed to have the constitution (V).

$$
\begin{array}{ccc}
& \text{CO} & \text{CO} \\
\text{(IV.)} \quad \text{N---CH} & & \text{PhN} \quad \text{CH} \\
\text{N} \quad \text{CH} & \text{CH·CH:NPh} & \text{CH} \quad \text{CH·CH:NPh (V.)} \\
\text{PhN} \quad \text{CO} & & \text{CO}
\end{array}
$$
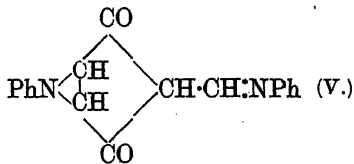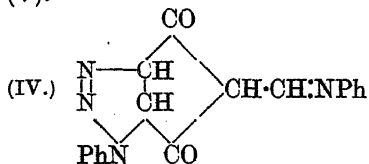
The first condensation product would be expected to contain two hydrogen atoms more than Wolff's compound (I). These, however, he suggested had been oxidised off by the excess of quinone used, thereby accounting for the presence of quinhydrone in the product of the reaction.

Somewhat similar results were obtained with α-naphthaquinone, but the initial triazole could not be isolated in a pure state.

The work described in the present paper was undertaken with the idea that the condensation would probably follow a simpler course with toluquinone, and that some of the doubtful points in Wolff's conclusions might be put to the test.

The action of azides on toluquinone yields first the anticipated triazoles; the azide reacting with only one double bond (and therefore probably not that contiguous to the methyl group) in the toluquinone molecule.

These triazoles are very unstable and cannot as a rule be isolated in a pure state, but pass with loss of nitrogen into compounds of the composition $R·C_7H_6O_2N$. There seems no reason to suppose that when loss of nitrogen occurs the six-carbon atom ring of the toluquinone nucleus becomes a five-atom ring, or that in the original product two hydrogen atoms have been removed by oxidation, since no trace of quinhydrone could be detected in the reaction products. It seems more likely that these substances should be

represented as containing rings of six and three atoms, respectively, having two carbon atoms in common. The formation and decomposition of the triazole may be represented thus :

$$
\begin{array}{ccc}
\text{CO} & \text{CO} & \text{CO} \\
\text{MeC} \quad \text{CH} & \text{MeC} \quad \text{CH--N} & \text{MeC} \quad \text{CH} \\
\text{HC} \quad \text{CH} \xrightarrow{+N_3R} & \text{HC} \quad \text{CH} \quad \text{N} \xrightarrow{-N_2} & \text{HC} \quad \text{CH} {>} \text{NR} \\
\text{CO} & \text{CO} \quad \text{NR} & \text{CO}
\end{array}
$$
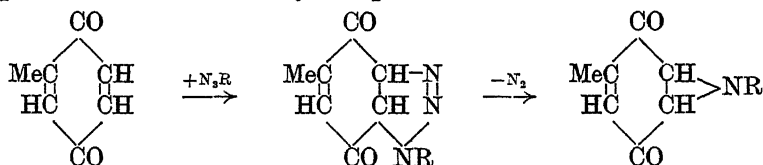
A series of these compounds has been prepared. The one obtained by the condensation of o-tolyl azide with toluquinone was found to be the most convenient for investigating the properties of the final product.

<div align="center">EXPERIMENTAL.</div>

Preparation of Toluquinone.—Toluquinone is easily made by the oxidation of o-toluidine by means of potassium dichromate, or manganese dioxide, and sulphuric acid (compare *Ber.*, 1887, **20**, 2283). The chief difficulty in the process is the isolation of the quinone from the reaction product. The following procedure has been found to yield the most satisfactory results.

A solution of 30 g. of o-toluidine in a mixture of 240 g. of concentrated sulphuric acid and 900 c.c. of water is well cooled in a freezing mixture, and stirred vigorously while 78 g. of finely powdered potassium dichromate are added slowly in portions of about 1 g. at a time. The stirring is continued for about ½ hour after all the dichromate has been added, and the mixture is kept for 12 hours. The toluquinone which separates is filtered off and distilled *in small portions at a time* in a current of superheated steam. The quinone suffers some decomposition when distilled, but this is reduced to a minimum by the method described, as the amount of decomposition appears to depend on the duration of the operation.

The azides required were prepared from the corresponding diazonium tetrachloroiodides as described by Chattaway, Garton, and Parkes (J., 1924, **125**, 1980).

Action of Phenyl Azide on Toluquinone and Formation of Phenylcycloiminotoluquinone.—A solution of 10 g. of toluquinone and 10 g. of phenyl azide in 30 c.c. of dry benzene was maintained at 50° for 20 hours. The dark brown solid that separated on cooling was washed with a little benzene, then repeatedly with ether to remove any unchanged toluquinone, and the buff-coloured residue of *phenylaziminotoluquinone* was recrystallised from warm acetone, in which it was fairly soluble, separating in small, yellow plates, m. p. 206° (darkening at about 190°) (Found : C, 64·9 ; H, 4·5 ; N, 17·4. $C_{13}H_{11}O_2N_3$ requires C, 64·7 ; H, 4·6 ; N, 17·4%).

On prolonged heating with benzene or on heating for a few minutes with aniline this compound loses nitrogen and passes into *phenyl*cyclo*iminotoluquinone*, which separates from boiling benzene in small, pale yellow needles, m. p. 130° (Found : C, 73·4 ; H, 5·2 ; N, 6·5. $C_{13}H_{11}O_2N$ requires C, 73·2 ; H, 5·1 ; N, 6·6%).

Action of o-*Tolyl Azide on Toluquinone.*—*o*-Tolylaziminotoluquinone, which must be the first product of the condensation of *o*-tolyl azide and toluquinone, is obtained as a microcrystalline powder, m. p. 155°, when equivalent quantities are heated together in chloroform solution. It cannot, however, be obtained perfectly pure, as it evolves nitrogen during recrystallisation.

If benzene be used instead of chloroform, owing to its higher boiling point, complete loss of nitrogen occurs during the heating and *o*-tolyl*cyclo*iminotoluquinone only is obtained.

Formation of o-*Tolyl*cyclo*iminotoluquinone.*—A solution of 20 g. of toluquinone (2 mols.) and 15 g. of *o*-tolyl azide (1 mol.) in 80 c.c. of benzene was heated under reflux for 10 hours. The benzene was then evaporated off and ether added to the dark brown, pasty residue, when *o*-tolyl*cyclo*iminotoluquinone separated as a yellow, microcrystalline powder, which was thoroughly washed with ether to remove any unchanged toluquinone. It was recrystallised several times from alcohol, then from benzene, and then once or twice more from alcohol. The pure product thus obtained crystallised from boiling alcohol, in which it was easily soluble, in golden-yellow needles, m. p. 139° (yield 7 g.).

This substance, which is without odour, is readily soluble in alcohol, benzene, or glacial acetic acid. It is characterised by marked stability towards reagents. It dissolves with a dark crimson colour both in sulphuric acid and in alcoholic potash. It is hydrolysed by boiling aqueous sodium hydroxide solution, yielding *o*-toluidine. It does not react with semicarbazide, phenylcarbimide, boiling aniline or phenol, nor with sodium hypobromite solution, nor is it reduced by tin and hydrochloric acid. It is unaffected by nitrous acid, and cannot be acetylated, showing that the compound does not contain an imino-group (Found : C, 74·3 ; H, 5·9 ; N, 6·3. $C_{14}H_{13}O_2N$ requires C, 74·0 ; H, 5·7 ; N, 6·2%).

It is evident from these results that the triazole first formed loses two atoms of nitrogen during the heating, thus becoming converted into *o*-tolyl*cyclo*iminotoluquinone.

This is confirmed by the results of analyses of similar substances obtained by condensing other aromatic azides with toluquinone.

Condensation of Other Azides with Toluquinone.—Other azides condense similarly when their solutions in dry benzene are boiled with toluquinone, but as a rule only the *cyclo*iminotoluquinones can

be isolated in a pure state owing to the instability of the corresponding aziminotoluquinones. They all separate from benzene or alcohol, in which they are moderately easily soluble, in small, yellow plates or needles.

p-*Chlorophenylcycloiminotoluquinone*, m. p. 180° (Found : Cl, 14·2. $C_{13}H_{10}O_2NCl$ requires Cl, 14·32%); 2 : 4-*dichlorophenylcycloiminotoluquinone*, m. p. 209·5° (Found : Cl, 25·2. $C_{13}H_9O_2NCl_2$ requires Cl, 25·15%); 2 : 5-*dichlorophenylcycloiminotoluquinone*, m. p. 229° (Found : Cl, 25·0%); p-*bromophenylcycloiminotoluquinone*, m. p. 185° (Found : Br, 27·1. $C_{13}H_{10}O_2NBr$ requires Br, 27·4%); 2 : 4-*dibromophenylcycloiminotoluquinone*, m. p. 216° (Found : Br, 43·1. $C_{13}H_9O_2NBr_2$ requires Br, 43·2%); 2 : 4 : 6-*tribromophenylcycloiminotoluquinone*, m. p. 171° (Found : Br, 53·7. $C_{13}H_8O_2NBr_3$ requires Br, 53·2%).

THE QUEEN'S, AND KEBLE COLLEGES,   [*Received, March 16th, 1925.*]
OXFORD.

CLXXIX.—*Compounds of Tervalent Molybdenum. Part III. New Oxalates.*

By WILLIAM WARDLAW and WILLIAM HENRY PARKER.

OF the metals chromium, molybdenum, tungsten, and uranium, only chromium has so far yielded oxalates of the tervalent element. This metal forms a hydrated normal oxalate, $Cr_2(C_2O_4)_3,xH_2O$, and complex salts of the types $R_2[Cr_2(C_2O_4)_4]$, $R_4[Cr_2(C_2O_4)_4(OH)_2]$, and $R_3[Cr(C_2O_4)_3]$; the potassium derivative of the last type has been resolved into its optically active components. Chilesotti (*Z. Elektrochem.*, 1906, **12**, 146), by electrolysis of a 3·5% solution of molybdenum trioxide in 2*N*-oxalic acid in a diaphragm cell, obtained an intensely yellowish-brown cathode liquid which, on concentration, with or without the addition of alkali oxalates, yielded no definite compounds. During the electrolysis a red powder, insufficient for analysis, separated in the cathode chamber. Although the stage of reduction could not be estimated accurately by titration against potassium permanganate owing to the presence of oxalic acid, such approximate titrations led Chilesotti to the conclusion that in oxalic acid, as in sulphuric and hydrochloric acids, molybdenum trioxide is not reduced electrolytically to a stage lower than the tervalent. Recently, Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 62, 458) attempted, without success, to isolate oxalates of tervalent molybdenum by dissolving in oxalic acid the hydroxide obtained by the action of ammonia on the complex salt

Y Y*

$K_3[MoCl_6]$, and concentrating the solution in a vacuum, alone or with addition of alkali oxalates.

In the present research, the hydroxide precipitated by the action of ammonia on the solution, containing tervalent molybdenum, produced by the electrolytic reduction of molybdenum trioxide in sulphuric acid was dissolved in oxalic acid, and the resulting solution electrolysed in a small diaphragm cell. When the cathode liquid was added to excess of pure, dry, air-free acetone, a well-defined *molybdenum oxyoxalate*, $Mo_2O(C_2O_4)_2,6H_2O$, separated. From this compound a more basic *salt*, $Mo_4O_3(C_2O_4)_3,12H_2O$, has been obtained. On exposure to the air in presence of moisture, these compounds are oxidised to the quadrivalent state, yielding bright red solutions from which, by precipitation in dry acetone, the *oxyoxalate* $MoO(C_2O_4),3H_2O$ has been obtained.

<div align="center">EXPERIMENTAL.</div>

Preparation of the Trihydroxide.—A solution of molybdenum trioxide (40 g.) in 54 c.c. of boiling sulphuric acid (d 1·84) containing a few drops of nitric acid was diluted, filtered, made up to a litre, and a portion (400 c.c.) electrolysed in a diaphragm cell with smooth platinum electrodes. The solution, containing tervalent molybdenum, was forced into a flask containing 75 c.c. of ammonium hydroxide (2·5N), and on addition to 2 litres of hot, air-free water the hydroxide separated as a black, flocculent precipitate, which was washed free from sulphate and ammonia; a sample, dried in a vacuum, was shown to contain tervalent molybdenum (J., 1924, **125**, 1911).

Preparation of the Soluble Oxyoxalate.—Oxalic acid crystals (50 g.) were covered with water to displace air, the suspension (300 c.c.) containing all the hydroxide prepared above was added, and the whole boiled in a rapid stream of nitrogen until the volume was 100 c.c. If the volume is reduced further, hydrolysis occurs with the separation of a dark precipitate. The golden-brown solution thus produced was cooled to room temperature, when the excess of oxalic acid crystallised. The supernatant liquid was filtered, electrolysed in a small diaphragm cell, C (Fig.), the cathode chamber of which was a large boiling tube and the anode chamber a tube of smaller bore closed at the lower end by a parchment membrane. The catholyte and anolyte consisted of the same liquid and the electrolysis was conducted for 12 hours at 4 volts and a current density of 0·05 amp. per sq. cm. at the cathode. The resulting golden-brown liquid was forced by nitrogen pressure into the precipitating bottle, P, containing a litre of pure, dry, air-free acetone, when the new *oxyoxalate* separated as a

finely-divided, brown powder which rapidly became granular.
This was washed with dry acetone and with dry ether, and dried,
first in a rapid stream of nitrogen and finally for a short period,
in situ, under reduced pressure. Prolonged drying in a vacuum
appears to cause decomposition of the compound. During all
these operations air was rigidly excluded.

Valency of the Molybdenum.—In the presence of oxalic acid it
is impossible to get a satisfactory end-point when titrating reduced
molybdenum solutions to the sexavalent state. The usual method
for determining the valency not being available, the following
procedure was adopted: A weighed quantity of the substance
dissolved in air-free sulphuric acid ($5N$) was titrated in the cold
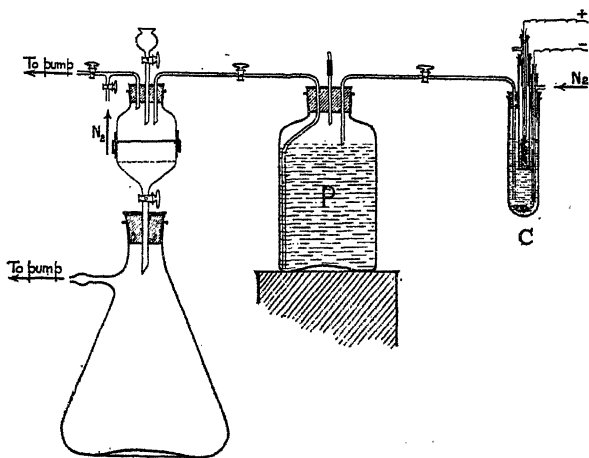
in a nitrogen atmosphere with standard permanganate. When
colourless, the solution was heated to 70° and the titration con-
tinued until a permanent pink colour was obtained. This reading
gives the amount of permanganate necessary to oxidise the molyb-
denum to the sexavalent state and to decompose the oxalate
radical. The permanganate required for the latter purpose was
estimated independently by warming a weighed quantity of the
salt in aqueous solution with 1 c.c. of nitric acid ($5N$) and pre-
cipitating the molybdenum as MoS_3. The filtrate was freed from
hydrogen sulphide by a rapid stream of carbon dioxide and titrated
at 70° with permanganate. By difference—calculated for the same
weight of material—the amount of permanganate required to
oxidise the molybdenum to the sexavalent condition is obtained,
and since 1 c.c. of $N/10$-permanganate $= 0.0032$ g. of Mo^{III}, the
percentage of molybdenum present in the salt can be deduced.

When this agrees with the results obtained by gravimetric analysis, the molybdenum is tervalent.

0.2436 g. gave 0.1437 g. MoO_3, corresponding to 39.32% Mo. 0.2436 g. required 29.54 c.c. of $KMnO_4$, corresponding to 38.80% Mo. Therefore valency $= 3$.

Analysis.—The molybdenum was estimated (*a*) by direct ignition of the oxyoxalate to the trioxide, (*b*) by precipitation as MoS_3 and subsequent ignition to the trioxide. The oxalate radical was estimated as described above, and the water by ignition of the salt in dry nitrogen and absorption of the moisture in sulphuric acid [Found: (*a*) Mo, 39.3; H_2O, 21.8; (*b*) C_2O_4, 35.9. Ratio $a : b = 1 : 0.996$. $Mo_2O(C_2O_4)_2,6H_2O$ requires Mo, 39.0; H_2O, 21.95; C_2O_4, 35.8%. Ratio $a : b = 1 : 1$].

Further confirmation of this formula was obtained by heating a known amount of the salt in pure dry nitrogen to 300°. The residue thus obtained was weighed and by further ignition in air converted into the trioxide. Under these conditions, the oxyoxalate was quantitatively decomposed to give the pentoxide with evolution of carbon monoxide, which was collected and shown to be free from carbon dioxide. At a higher temperature some carbon dioxide was evolved and the residue contained a lower oxide.

0.2132 g. gave 0.1179 g. of residue (X) and 0.1248 g. of trioxide (Y). 0.2780 g. gave 0.1537 g. of residue (X) and 0.1634 g. of trioxide (Y). Ratio X/Y: Found, 0.941, 0.945; calc., 0.944.

The decomposition proceeds, therefore, in accordance with the equation $Mo_2O(C_2O_4)_2,6H_2O = Mo_2O_5 + 4CO + 6H_2O$.

Properties and Reactions.—The oxyoxalate is brown and dissolves readily in cold water to give a golden-brown solution which gradually undergoes oxidation in the air, the colour changing to bright red. Hydrolysis occurs in the slightly warmed solution with separation of a reddish-brown precipitate, probably the insoluble oxyoxalate. The new solid is very unstable in air and does not dissolve in the usual organic solvents. From the aqueous solution the oxalate radical is not precipitated by calcium chloride nor the molybdenum by alkalis in the cold, indicating the presence of a complex ion. On warming, however, a reddish-brown precipitate appears in the first case and the black hydroxide in the second. The solution has powerful reducing properties, precipitating the metal from solutions of copper and silver salts. Ferric salts are reduced to the ferrous condition. On warming with concentrated sulphuric acid the solid gives a beautiful purple solution, which on dilution with water becomes greenish-yellow and has pronounced reducing properties.

Preparation of the Insoluble Oxyoxalate.—If the electrolysis is

continued for more than 12 hours a brick-red powder gradually separates in the cathode chamber. This was noted by Chilesotti in his experiments on the electrolytic reduction of solutions of molybdenum trioxide in oxalic acid. A similar substance has now been prepared in quantity by prolonged boiling of the solution of molybdenum trihydroxide in oxalic acid. The solid was washed by decantation with air-free water and dried in the special apparatus shown in the figure after further treatment with alcohol and dry ether. Analysis by the methods already described showed the molybdenum to be tervalent, and the compound to have the formula $Mo_4O_3(C_2O_4)_3,12H_2O$ [Found: (a) Mo, 42·2, 41·9; (b) C_2O_4, 28·8, 28·8. Ratio $a : b = 1 : 0·746$, $1 : 0·75$. $Mo_4O_3(C_2O_4)_3,12H_2O$ requires Mo, 42·1; C_2O_4, 28·95%. Ratio $1 : 0·75$].

During the preparation of this substance carbon dioxide and carbon monoxide were evolved from the boiling solution. The residue obtained by igniting the compound in a current of pure dry nitrogen was bluish-black and pyrophoric and on exposure to air was converted spontaneously into the pentoxide. The composition of the residue varies with the temperature of decomposition, which may occur in two main ways :—

(1) $Mo_4O_3(C_2O_4)_3 = 2Mo_2O_3 + 3CO + 3CO_2$.

(2) $Mo_4O_3(C_2O_4)_3 = 2MoO_2.Mo_2O_5 + 6CO$.
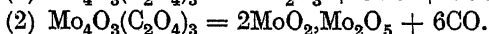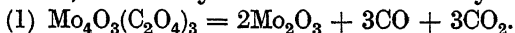
By carrying out the ignition in a short piece of combustion tubing fitted with glass taps, it was possible to weigh the pyrophoric residue, and, on admission of air, to determine the weight of Mo_2O_5 obtained from it. This gave the trioxide on further heating in air. It was hoped to obtain the sesquioxide according to equation (1), but this was found impossible. The residue obtained at 300° was Mo_4O_9 and under these conditions only carbon monoxide was evolved, the decomposition proceeding according to equation (2). At still higher temperatures, some carbon dioxide was formed and the residue varied in composition, but approximated to MoO_2, according to the reaction $Mo_4O_3(C_2O_4)_3 = 4MoO_2 + 5CO + CO_2$. The relative volumes of the gases evolved were in agreement with the residues obtained and afford a confirmation of the empirical formula deduced from analysis.

Properties and Reactions.—The pure dry product is bright reddish-brown and insoluble in water and the usual organic solvents. Hot concentrated hydrochloric acid and cold concentrated sulphuric acid dissolve it readily to give reddish-brown solutions, whilst warm dilute nitric acid produces a bright red solution which on boiling is decolorised through oxidation. A suspension of the insoluble oxyoxalate in water shows the same reducing properties as the soluble oxyoxalate. Alkalis do not dissolve it, but

change its colour to reddish-violet in the cold and black on heating.

Molybdenyl Oxalate.—The golden-brown solution prepared electrolytically undergoes gradual oxidation on exposure to the air and becomes carmine-red. If this solution is concentrated carefully on a water-bath, and the excess of oxalic acid crystallised, the filtrate yields in acetone a pinkish-red powder which on washing with alcohol and drying over phosphoric oxide contains quadrivalent molybdenum and has the composition $MoO(C_2O_4),3H_2O$. Its formation under these conditions may be represented thus : $Mo_2O(C_2O_4)_2 + \frac{1}{2}O_2 + .H_2O = 2MoO(C_2O_4) + H_2O$. This is comparable with the transformation of the double cyanide, $K_3[Mo(CN)_6]$, of tervalent molybdenum, to $K_4[Mo(CN)_8]$, containing quadrivalent molybdenum, by air oxidation in the presence of water in accordance with the equation $K_3[MoCl_6] + \frac{1}{2}O_2 + \frac{1}{2}H_2O + 8KCN = K_4[Mo(CN)_8] + 6KCl + KOH$. Owing to the complete solubility of this oxalate in water without decomposition the molybdenum could be precipitated quantitatively from the hot solution by potassium hydroxide as the black hydroxide, which was weighed as MoO_3 after ignition in air. The oxalate radical was estimated in the acidified filtrate by titration with permanganate. The molybdenum was also determined by direct ignition of the oxalate to the trioxide [Found : (*a*) Mo, 37·75 ; (*b*) C_2O_4, 34·7 ; H_2O, 21·0. Ratio $a : b = 1 : 0·996$. $MoOC_2O_4,3H_2O$ requires Mo, 37·8 ; C_2O_4, 34·65 ; H_2O, 21·3%. Ratio 1 : 1].

By ignition of the compound in a current of pure dry nitrogen a black residue corresponding to the dioxide was obtained, the decomposition proceeding according to the equation $MoOC_2O_4 = MoO_2 + CO + CO_2$ [0·0932 g. of residue (X) gave 0·1048 g. of MoO_3 (Y). Ratio X : Y, found 0·890 ; calc., 0·889].

Properties of Molybdenyl Oxalate.—The red powder as prepared above is extremely hygroscopic, and very soluble in water, producing a magenta-coloured solution which appears quite stable in the air. From the freshly-prepared solution, which has a pronounced acid reaction, the oxalate radical is not precipitated by calcium chloride nor the molybdenum by alkalis in the cold, which render the solution bluer. The presence of a complex ion in this oxalate of quadrivalent molybdenum, together with its acidic properties and the colour changes produced by alkalis, suggests its formulation as $\left[Mo\, \genfrac{}{}{0pt}{}{O_2}{2H_2O}\, C_2O_4 \right]H_2$.

Experiments now in progress indicate the existence of two salts corresponding to this dibasic acid. The aqueous solution slowly deposits silver and copper from solutions of their salts, whilst ferric

salts are immediately reduced to the ferrous condition. These reducing properties are not so pronounced as those of the oxalates of tervalent molybdenum.

Conclusion.

So far, no compound of molybdenum is known certainly to produce a tervalent molybdenum ion. The new soluble oxyoxalate shows remarkable similarity in its properties and mode of decomposition to the oxysulphate previously described (J., 1924, **125**, 1910).

$$Mo_2O(SO_4)_2,6H_2O = Mo_2O_5 + 2SO_2 + 6H_2O.$$

$$Mo_2O(C_2O_4)_2,6H_2O = Mo_2O_5 + 4CO + 6H_2O.$$
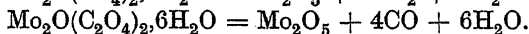
In both these compounds, the molybdenum is present as a complex ion and they may be represented by the formulæ

$$3H_2O{\cdot}XO_4{:}Mo{\cdot}O{\cdot}Mo{:}XO_4{\cdot}3H_2O \quad \text{or} \quad \left[3H_2O{\cdot}Mo{\Big\langle}{\overset{XO_4}{\underset{XO_4}{-O-}}}{\Big\rangle}Mo{\cdot}3H_2O \right]$$
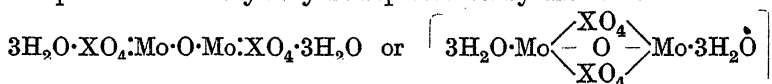
where $XO_4 = SO_4$ or C_2O_4. A further possibility would be to consider these substances as dibasic acids of the formula $\left[Mo{\overset{O}{\underset{3H_2O}{}}}XO_4 \right]_2 H_2$. The ease with which they hydrolyse and oxidise in aqueous solution renders conductivity measurements of little significance. There seems to exist a distinct analogy between the chromium salt, $2R_2C_2O_4,Cr_2(C_2O_4)_2(OH)_2$, and the new oxyoxalate, $Mo_2O(C_2O_4)_2$. Werner (*Annalen*, 1914, **406**, 261) assigned to this double chromium oxalate the constitution

$$\left[(C_2O_4)_2Cr{\Big\langle}{\overset{OH}{\underset{OH}{}}}{\Big\rangle}Cr(C_2O_4)_2 \right]R_4,$$
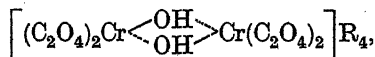
of which the free acid would be $\left[(C_2O_4)_2Cr{\Big\langle}{\overset{OH}{\underset{OH}{}}}{\Big\rangle}Cr(C_2O_4)_2 \right]H_4$. Owing probably to its great instability, this substance has not been isolated, but a probable decomposition product would be the analogue of the molybdenum oxyoxalate,

$$\left[2H_2O(C_2O_4)Cr{\Big\langle}{\overset{OH}{\underset{OH}{}}}{\Big\rangle}Cr(C_2O_4)2H_2O \right].$$
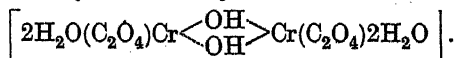
In this formula, only five molecules of water are represented in the co-ordination sphere. The formation of the insoluble oxyoxalate from the soluble salt by warming its aqueous solution takes place with separation of oxalic acid, detected by its ionic reactions. This change may be symbolised as follows :

$$2Mo_2O(C_2O_4)_2 + H_2O = Mo_4O_3(C_2O_4)_3 + H_2C_2O_4.$$
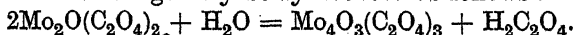
The relationship which exists between the new oxalate of quadrivalent molybdenum and the known derivatives of the quinque- and sexa-valent element is clearly seen from the co-ordination

formulæ for these substances. The compounds of sexavalent molybdenum comprise the free acid and its salts,

$$\left[\text{Mo}\,\frac{O_3}{C_2O_4}\right]H_2, \text{R′H, R′}_2.$$
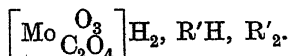
The derivatives of the quinquevalent element are known only as salts, $\left[\text{Mo}\,\frac{O_2}{C_2O_4}\right]\text{R′}$, whilst the oxalate of quadrivalent molybdenum now prepared is probably $\left[\text{Mo}\,\frac{O_2}{C_2O_4}\,2H_2O\right]H_2.$

Summary.

(1) By electrolytic reduction of a solution of the trihydroxide of molybdenum in oxalic acid and precipitation in acetone an oxyoxalate of tervalent molybdenum, $Mo_2O(C_2O_4)_2,6H_2O$, has been obtained.

(2) Decomposition of the above oxalate or prolonged boiling of a solution of the trihydroxide in oxalic acid yields the insoluble oxyoxalate, $Mo_4O_3(C_2O_4)_3,12H_2O$.

(3) Air oxidation of these compounds in presence of water yields a red solution which gives with alcohol a precipitate of molybdenyl oxalate, $MoO(C_2O_4),3H_2O$, and is being further studied.

(4) The oxalate radical is present as a complex ion.

CLXXX.—Bromination of 4′-Amino-1-phenyl-5-methyl-benzthiazole and of 1:1-Bisbenzthiazole.

By ROBERT FERGUS HUNTER.

THE dibromo-addition compound formed from dehydrothiotoluidine (4′-amino-1-phenyl-5-methylbenzthiazole) by bromination in glacial acetic acid (Gattermann, *Ber.*, 1889, **22**, 422) cannot have the constitution $C_6H_3Me\left<\frac{S\text{——}}{NBr}\right>CBr\cdot C_6H_4\cdot NH_2$, for it lacks the explosive properties normally associated with the presence of the group :NBr (Spencer, this vol., p. 216) and is relatively stable to air, boiling water, dilute alkalis, etc. Since the action of sulphurous acid or sodium hydrogen sulphite instantly reconverts it into dehydrothiotoluidine, hydrogen bromide being evolved, the com-

pound is a perbromide, although of unusual stability, the most probable constitution being $C_6H_3Me{<}{\overset{\text{S}}{\underset{\text{NBr}_2}{}}}{>}C·C_6H_4·NH_2$.

Similarly, the *tetrabromo*-addition compound of 1 : 1-bisbenzthiazole and bromine is a perbromide, probably of the constitution $C_6H_4{<}{\overset{\text{S}}{\underset{\text{NBr}_2}{}}}{>}C·C{<}{\overset{\text{S}}{\underset{\text{NBr}_2}{}}}{>}C_6H_4$, for it also is instantaneously reduced to the parent bisbenzthiazole on treatment with sulphurous acid; moreover, it loses its bromine on mere exposure to the air or in boiling alcohol containing a trace of alkali.

EXPERIMENTAL.

In the preparation of 4′-amino-1-phenyl-5-methylbenzthiazole a mixture of alcohol and benzene (1 : 1) is a much better solvent than the alcohol and acetone formerly used (*J. Soc. Chem. Ind.*, 1923, **42**, 302).

In the preparation of the dibromide the acetic acid (Gatterman, *loc. cit.*) was replaced by chloroform, from which the dibromide separated in dark red-brown granules, which were dried in a vacuum over potassium hydroxide; m. p. 190° (sintering). Yield quantitative. The dibromide cannot be diazotised, treatment with nitrous acid causing evolution of bromine and production of highly resinous products.

1 : 1-*Bisbenzthiazole.*—1-Chlorobenzthiazole (Hofmann, *Ber.*, 1879, **12**, 1126) was recovered unchanged after being heated under reflux with sodium in dry ether.

A mixture of acetanilide and sulphur (Hofmann, *Ber.*, 1880, **13**, 1223) was heated at its b. p. for 30 hours, pale yellow needles of bisbenzthiazole subliming. The product was extracted with 60% sulphuric acid (Lauth, *Bull. Soc. chim.*, 1896, **15**, 82), and the crude base heated under reflux with alcohol. Sublimation of the base, although yielding a pure product, involves very heavy losses due to carbonisation. The compound is very sparingly soluble in all ordinary solvents and in nitrobenzene or aniline, but dissolves readily in tetrachloroethane. Purification by crystallisation from alcohol is quite ineffective, although described in the original paper (*loc. cit.*). The substance crystallises from absolute alcohol-tetrachloroethane in fine, colourless crystals which do not melt below 300°.

Bromination.—The base was recovered unchanged after treatment in alcoholic suspension with excess of bromine.

The bisbenzthiazole (2 g.) suspended in 40 c.c. of chloroform was slowly treated with 4 c.c. of bromine; after ½ hour the mixture was warmed on a water-bath, when the bulk of the solid dissolved. The

solution was filtered, concentrated, and cooled; on scratching, red-brown needles of the *tetrabromide* separated which were dried on a porous tile in a vacuum. It becomes pale yellow and loses bromine at about 170°, but the actual melting point appears to be above 300° (Found : Br, 52·9. $C_{14}H_8N_2Br_4S_2$ requires Br, 54·5%). The tetrabromide loses bromine while it is being weighed.

In conclusion the author desires to express his gratitude to Prof. J. F. Thorpe and Dr. M. A. Whiteley for their kind interest in this work.

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CLXXXI.—*The Decomposition of Hydrogen Peroxide by Cobaltic Hydroxide.*

By FREDERICK GERALD TRYHORN and GILBERT JESSOP.

HYDROGEN peroxide is very slowly decomposed in neutral solution by a suspension of cobaltic hydroxide. Traces of alkali, of themselves too small to cause decomposition, greatly increase the activity of the hydroxide. Velocity coefficients for such a reaction calculated on the basis of a monomolecular decomposition of the peroxide are unsatisfactory. Thus Bredig and his collaborators (*Z. physikal. Chem.*, 1899, **37**, 258; *Ber.*, 1904, **37**, 798), using cobalt hydroxide and colloidal platinum, found a steady rise of the constant in the presence of alkali, for which no satisfactory explanation has been offered. Occasion arose to investigate further this reaction, since the catalase-like action of many cobaltammine salts in decomposing hydrogen peroxide (Shibata and Kaneko, *J. Chem. Soc. Japan*, 1923, **44**, 166) has been found to be due to cobaltic hydroxide produced by slow hydrolysis of the cobaltammine ions.

EXPERIMENTAL.

The decomposition of the hydrogen peroxide was followed by determining the rate of evolution of oxygen at constant pressure. Reaction occurred in a glass bulb of about 40 c.c. capacity which could be connected by a three-way tap to either of two 5-c.c. gas burettes provided with levelling bulbs and calibrated gravimetrically. By these means oxygen collected in one burette could be measured accurately while the other burette was filling. During the experiments, in all of which Merck's " perhidrol " (unstabilised), freshly diluted with conductivity water and estimated by titration,

was used, the bulb was vigorously agitated by means of a motor, and the whole of the apparatus was immersed in a thermostat at $25 \pm 0.02°$. In one or two series of experiments in which readings were required at long time intervals the titration method was used.

Cobaltic hydroxide was prepared by the addition of ammonia to a mixture of hydrogen peroxide and cobalt chloride solution. Suitably low concentrations of these reagents gave a stable brown sol; higher concentrations gave unstable sols which soon coagulated. In these cases, the hydroxide was shaken into a coarse suspension and used as such. In all but the preliminary experiments, for reasons referred to later, the catalyst preparations were treated with an excess of hydrogen peroxide before use. Some comparison experiments were made with a suspension of cobalt peroxide prepared by Howell's method (*Proc. Roy. Soc.*, 1923, *A*, **104**, 134). This was unstable in presence of hydrogen peroxide, changing immediately from black to the characteristic brown colour of the cobaltic hydroxide preparations, and showing the catalytic behaviour of these.

Table I gives the reactant concentrations in the experiments quoted. All concentrations are expressed in millimoles per litre of reaction mixture. The letters *a*, *b*, *c*, indicate successive additions of hydrogen peroxide to the same reaction mixture.

Results.

The treatment of the results has been based on the equation for a catalysed monomolecular reaction, $dx/dt = kA(a - x)$. Integration over a small time interval, during which the activity of the catalyst may be regarded as constant, gives

$$kA = 1/(t_2 - t_1) . \log \{(a - x_1)/(a - x_2)\},$$

where $a - x_1$ and $a - x_2$ are the reactant concentrations at the times t_1 and t_2. Provided, as was the case in these experiments, the time interval is small, the calculated value of kA, which has been used as a measure of the catalyst activity, becomes very nearly the true value at the mean time $(t_2 + t_1)/2$.

The curves in Fig. 1, for some preliminary experiments, indicate the changes in activity of a given mass of catalyst. In these experiments, two or more portions of hydrogen peroxide were decomposed successively in presence of traces of ammonia by one portion of catalyst, the second portion of peroxide being added as soon as the first reaction had ceased. During the first part of each experiment the activity fell, passed through a minimum, and then rose, either rapidly or slowly. In the latter parts of the experiments the initial fall of activity was absent, the new curve lying below the previous one, and showing a rise of activity as the

hydrogen peroxide concentration decreased.   The activity appears
subject to a dual change : an irreversible fall, and a simultaneous
reversible increase inversely dependent on the hydrogen peroxide
concentration.

The irreversible fall was at first attributed to aggregation of
particles of cobaltic hydroxide.   The fact that this fall was not
eliminated, or even appreciably diminished, when the catalyst was
protected by gelatin or adsorbed on kieselguhr shows that it is
not due to aggregation.   It could, however, be made negligible in

FIG. 1.
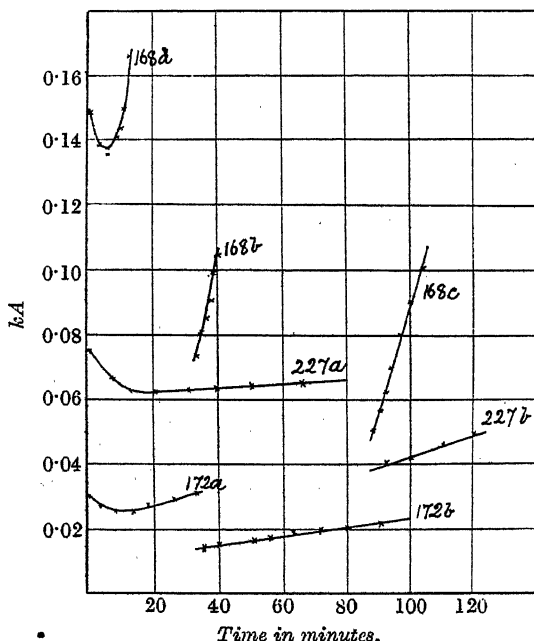
two ways; by treating the catalyst with excess of hydrogen per-
oxide, or by allowing it to form very slowly by the hydrolysis of a
cobaltammine salt.

These facts suggest that the irreversible fall in activity is due
to a change in the nature of the catalyst surface.   When the
hydroxide particles are formed as the result of a sudden molecular
condensation, it may happen that the surface molecules are deposited
at so rapid a rate that they do not orient themselves in positions
of minimum potential energy.   If during catalysis such a surface
adsorbs hydrogen peroxide, the operation of the adsorptive forces
may so disturb or weaken the cohesive forces binding the cobaltic

hydroxide molecules together that on decomposition of the peroxide the loosened hydroxide can rearrange itself on the surface in a position of minimum potential energy. If, as seems likely, the stable orientation of the surface molecules corresponds with a minimum activity, the catalyst will suffer an irreversible fall of activity to a value constant for a given hydrogen peroxide concentration. When, on the other hand, the hydroxide aggregates are formed as a result of a slow hydrolytic process, each molecule will be deposited in a position of minimum potential energy, and the irreversible fall of activity should be absent, in agreement with experiment.

FIG. 2.

Millimoles of ammonia.

Millimoles of catalyst, as cobalt.

Millimoles per litre of hydrogen peroxide.
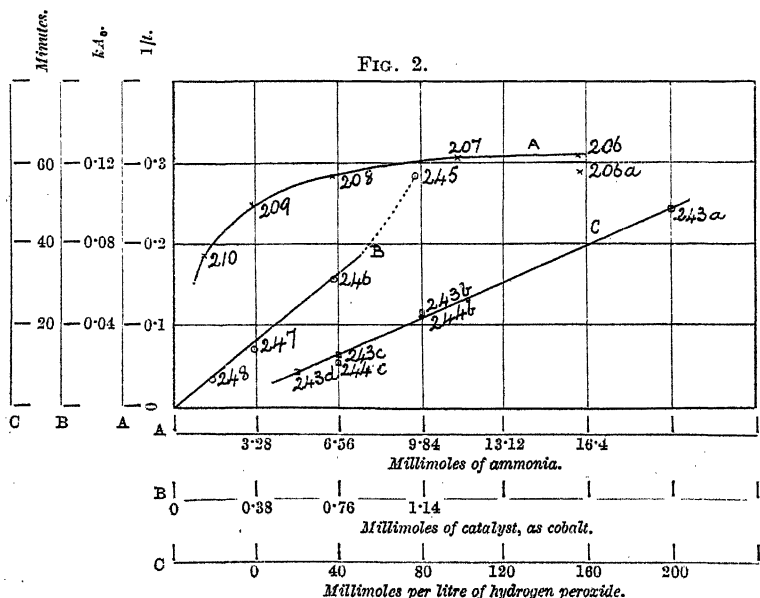
Though the forms of the curves in Fig. 1 were easily reproducible, similar experiments were not reproducible numerically to within less than about 5%. This difficulty was overcome by treating the catalyst preparation with excess of hydrogen peroxide to prevent the irreversible fall of activity. Reproducibility to within 2% was thus secured. Catalyst so treated was then used to investigate the effect of varying individually the amounts of catalyst, ammonia, and hydrogen peroxide in the reaction, with the following results.

I. Curve A, Fig. 2, shows the influence of small amounts of ammonia on the catalytic decomposition of hydrogen peroxide by a fixed amount of catalyst. To make the results comparable, the reciprocals of the time of evolution of 20 c.c. of oxygen (at 25°

and 760 mm. pressure) are plotted against ammonia concentrations. The ordinates are thus measures of the catalyst activity during a fixed portion of the reaction. The activity is increased on addition of ammonia, rapidly at first and then slowly towards a constant value. Check experiments without catalyst showed that the highest ammonia concentrations used in this series produced no measurable decomposition of the peroxide during the period of an experiment. This promoter effect is attributable to the influence of hydroxyl ions, since by adding ammonium chloride to repress the ionisation of the ammonium hydroxide the activity of the catalyst was sharply depressed. At still higher ammonia concentrations, a fall of activity was indicated, attributable to partial solution of the catalyst, in agreement with the results of Clarens (*Bull. Soc. chim.*, 1923, **33**, 280).

II. The initial activity of the catalyst in a series of experiments using varying amounts of catalyst is shown in curve B, Fig. 2. These values were obtained by extrapolating the experimental activity curves to zero time. The concentrations of catalyst varied from 1·12 to 0·19 millimoles per litre (calculated as cobalt). The initial concentrations of ammonia and hydrogen peroxide were kept constant. At low concentrations of catalyst the initial activity is proportional to its amount. At higher concentrations the activity appears to increase more rapidly than the catalyst concentration. The value for experiment 245 is open to doubt, since the reaction was extremely rapid in this high concentration, reaching completion in 8 or 9 minutes.

III. Curve C, Fig. 2, illustrates the effect of hydrogen peroxide concentration on the catalyst activity. Reaction mixtures were made containing similar concentrations of catalyst and ammonia, while the hydrogen peroxide varied over a tenfold concentration range. These experiments were made by the titration method, as readings were required at comparatively long intervals. The time necessary for a 10% decomposition of the hydrogen peroxide was taken as a measure of the catalyst activity. The catalyst activity varies inversely as the time of decomposition of a given portion of the peroxide. From the curve the activity may be seen to be an inverse linear function of the initial hydrogen peroxide concentration.

Discussion.

Freundlich (" Kapillarchemie," 380 *et seq.*) attributed the rise of activity of colloidal platinum in decomposing hydrogen peroxide to the change of the hydroxyl-ion concentration during reaction. An investigation of this suggestion has shown that the rise of activity persisted in reaction mixtures in which the hydroxyl-ion concen-

TABLE I.

Experiment.	Catalyst (as cobalt).	Ammonia.	Ammonium chloride.	Hydrogen peroxide.
168a, b, c.	0·133	6·54	0·266	63·6, 62·3, 59·8
172a, b.	0·0533	6·54	0·1066	65·0, 68·0
173b, 174b.	0·12	6·54	0·24	60·5, 76·5
175b.	0·133	6·54	0·266	74·8
197b.	0·28	11·45	0·56	55·8
206, 207.	—	16·40, 11·48	—	62·5, 62·1
208, 209.	0·14	6·56, 3·28	0·28	62·2, 62·4
210, 227a.	—	1·13, 16·40	—	61·7, 71·7
227b.	—	16·40	—	54·6
231b, 235a.	0·28	16·40, 13·12	17·23	47·7, 65·5
235b, 235c.	—	13·12, 16·40	—	65·6, 64·1
238b.	0·28	6·54	0·56	65·8
240b, 241b.	0·28	16·40	16·40	66·3, 62·3
243a, 243b.	0·056	16·40	16·40	170·7, 85·3
243c, 243d.	—	—	—	41·0, 20·3
244b, 244c.	—	—	—	85·3, 41·0
245, 246.	1·12, 0·75	16·40	16·40	65·7, 66·1
247, 248.	0·373, 0·19	—	—	69·3, 68·3
249b, 250b.	CoO₂	16·40	16·40	41·7, 52·3
	Platinum			
	catalyst.			
251.	0·0194	—	—	60·4
252a, b, c.	0·0485	—	—	57·0, 51·7, 54·1
263a, b.	0·0383	—	—	65·0, 67·1
	Palladium	NaOH		
	catalyst.	(Bredig and Fortner).		
VII	0·001	0·003	—	100·0
VIII, IX	0·064, 0·016	16·0	—	100·0
X	0·004	—	—	—

tration was made constant by Washburn's method (*J. Amer. Chem. Soc.*, 1908, **30**, 37).

It was not found possible to interpret the observed facts by any purely chemical mechanism of reaction. The more probable mechanism is that the decomposition of the peroxide occurs in an adsorbed film at the cobalt hydroxide surface. Application of Freundlich's adsorption equation requires a linear relation between log $1/kA$ and log $(a - x)$. Whilst this relationship held over some portion of many reactions, in no case was it applicable to a complete reaction.

The use of the Freundlich equation implies that there is no upper limit to the amount of hydrogen peroxide adsorbable by a given amount of cobaltic hydroxide. This leads to the conclusion that in any but extremely weak solutions the adsorbed film must be many molecules in thickness. Langmuir has adduced evidence (*Trans. Faraday Soc.*, 1922, **17**, 607) that the surface attractive forces are operative only over distances of the order of atomic diameters, and that adsorption ceases after the formation of a monomolecular layer. A treatment of the present results on this basis by the method used by Langmuir (*loc. cit.*, p. 621) has proved

more satisfactory.   The following mechanism is therefore suggested for the reaction.

Adsorption of hydrogen peroxide molecules on the catalyst surface, at a rate proportional to their concentration in the reaction mixture, causes a redistribution of the intramolecular force fields in the adsorbed molecules, resulting in an increased tendency to ionise of one hydrogen atom.   This may be visualised as due to a dragging of the electron sheaths of the oxygen atoms towards the adsorbing surface with the result that the repulsion between the oxygen nuclei and hydrogen nuclei is enhanced.   This " loosened " hydrogen ion is then removed as water on the impact of a hydroxyl ion, leaving the unstable ion O_2H' adsorbed on the surface.   This mechanism accounts in a simple way for the form of curve A, Fig. 2.   The average life of an adsorbed hydrogen peroxide molecule in low hydroxyl-ion concentrations may be comparatively long; addition of alkali increases the rate of collision of hydroxyl ions with adsorbed peroxide molecules, the average life of which is thereby shortened.   This will approach to a minimum value when so much alkali has been added that the rates of impact of hydroxyl ions and of adsorption of peroxide molecules are equal.   Increase of alkali beyond this limit will be without further effect unless dissolution of the catalyst is caused.   The O_2H' ions left on the catalyst are unstable and decompose, regenerating hydroxyl ions and leaving atomic oxygen on the surface.   If, as seems probable, the tendency for atomic oxygen to revert to the molecular form is greater than its tendency to form an adsorption complex with the catalyst, molecular oxygen will be formed.   This mechanism may be represented graphically thus :—

$$S \vdots O = O \genfrac{}{}{0pt}{}{H}{H} + OH' \; \rightarrow \; S \vdots O = O \diagdown_H{}' + H_2O \rightarrow S + \tfrac{1}{2}O_2 + OH'$$
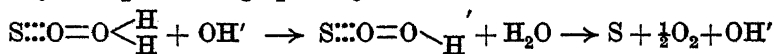
where S indicates the catalyst surface.

The portion of the catalyst surface concerned in the above changes is to be regarded as the active surface.   This is not necessarily the whole of the surface.   If the possibility of selective adsorption is admitted, a large part of the total surface must be considered as occupied by water molecules.   Since the concentration of these does not appreciably change during reaction, the surface so occupied, and also the active surface, may be regarded as constant.

The active surface at any moment may be regarded as partly free and partly occupied by peroxide molecules and ions.   If θ_1, θ_2, represent the fractions of the active surface which are occupied by peroxide molecules and ions, and θ_3 the free active surface, then

$$\theta_1 + \theta_2 + \theta_3 = 1 \quad . \quad . \quad . \quad . \quad (1)$$

Assuming that the rates of impact of peroxide molecules and of hydroxyl ions on unit surface of the catalyst are proportional to their concentrations in solution, we may write the following expressions for " rates of reaction " per unit area of the catalyst surface,

Rate of condensation of peroxide molecules $= \alpha_1 c_1$
Rate of decomposition of adsorbed molecules $= \alpha_2 c_2$
Rate of decomposition of peroxide ions $= \alpha_3$

where α_1, α_2, α_3 are constants and c_1 and c_2 are the concentrations of hydrogen peroxide and hydroxyl ions in solution. For a steady state the actual rates of the above reactions are equal and

$$\alpha_1 \theta_3 c_1 = \alpha_2 c_2 \theta_1 = \alpha_3 \theta_2 \quad . \quad . \quad . \quad . \quad (2)$$

Here, $\alpha_3 \theta_2$ is the rate of formation of atomic oxygen per unit active surface. If the polymerisation of this to molecular oxygen is regarded as instantaneous, the corresponding rate of evolution of gaseous oxygen is $\frac{1}{2}\alpha_3 \theta_2$. For a catalyst of total active surface S the observed rate of reaction becomes $\frac{1}{2}S\alpha_3 \theta_2 = dx/dt$. Eliminating θ_1, θ_3 in (1) by means of (2) and writing

$$\alpha_3 \theta_2 = \frac{2dx/dt}{S}, \text{ we get } \frac{2}{S}\frac{dx}{dt}\left[\frac{1}{\alpha_1 c_1} + \frac{1}{\alpha_3} + \frac{1}{\alpha_2 c_2}\right] = 1.$$

For c_1 we may write $(a - x)$ and so obtain

$$\frac{(a - x)}{dx/dt} = \frac{1}{kA} = \frac{2}{S}\left[(a - x)\left\{\frac{1}{\alpha_2 c_2} + \frac{1}{\alpha_3}\right\} + \frac{1}{\alpha_1}\right] \quad . \quad . \quad (3)$$

This equation may be tested in several ways.

A. The rise in the ordinary monomolecular velocity coefficient is accounted for by the fact that it is measured by the term $1/(a - x) . dx/dt$. According to the mechanism suggested above, the value of dx/dt will remain constant so long as there is present sufficient hydrogen peroxide to maintain the adsorption equilibrium, although the value of $(a - x)$ is steadily decreasing. Thus the value of $1/(a - x) . dx/dt$ will increase.

B. In any given experiment in which S and c_2 are constant, equation (3) reduces to

$$1/kA = k_1(a - x) + k_2 \quad . \quad . \quad . \quad . \quad (4)$$

Thus $1/kA$ should be a linear function of $(a - x)$. We may regard c_2, the hydroxyl-ion concentration, as constant so long as it lies in the region where further increase is without effect on the catalyst, or in experiments in which it is regulated by the addition of ammonium chloride. Fig. 3 illustrates the application of this test to a number of experiments in which these conditions held, and in which the irreversible fall in activity had been eliminated

by previous treatment of the catalyst with hydrogen peroxide.   In every case a satisfactory linear relation is obtained.

C. The form of curve A, Fig. 2, follows from equation (3), if the concentration of hydroxyl ions in very dilute ammonia solutions is regarded as proportional to the ammonia concentration; for, when S and $(a - x)$ are constant, (3) reduces to $kA = nc_2/(1 + mc_2)$, where n and m are constants.

D. When $(a - x) = 0$, $1/kA = k_3S$.   Thus, when successive portions of hydrogen peroxide are decomposed by a catalyst of constant active surface, the $1/kA$ curves should converge when $(a - x) = 0$, irrespective of the hydroxyl-ion concentration.   It was not possible to satisfy this test experimentally in many cases,

FIG. 3.
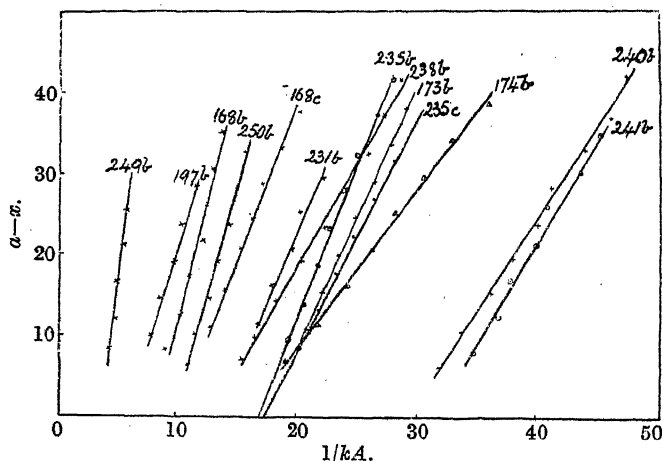
since any slight aggregation or surface change in the catalyst will greatly affect the convergence points of the curves.   Fig. 3 includes one pair of experiments (235b, 235c) in which the necessary conditions were fulfilled.   This test seems easier to realise in the case of catalysis by colloidal platinum (experiments 252a, b, c, Fig. 4). This is to be expected, since surface changes are less probable when dealing with metal particles.

E. When $(a - x)$ and c_2 are constant, equation (3) reduces to $1/kA = k_4/S$—or, in experiments with constant hydrogen peroxide and ammonia concentrations, the initial activity should be proportional to the active surface, and therefore to the amount of catalyst.   This relationship is realised for low concentrations of catalyst in curve B, Fig. 2.

Since the mechanism suggested for the present reaction is inde-

pendent of the chemical nature of the catalyst, equation (4) was further tested by applying it to some data of Bredig and Fortner (*Ber.*, 1904, **37**, 798) for the decomposition of hydrogen peroxide by alkaline palladium sol. Monomolecular velocity coefficients calculated by them showed a rise, in many cases as much as 25%, during the reaction.

Curves VII—X, Fig. 4, refer to some of these experiments, in which the reactant concentrations were those given in Table I. To bring these curves into suitable positions in Fig. 4, the actual values of $(a - x)$ have been multiplied by 5, and the values of $1/kA$ divided by 20, 5, 2, and 2, respectively. Except in the initial stages of the reactions, equation (4) applies with reasonable accuracy.

FIG. 4.
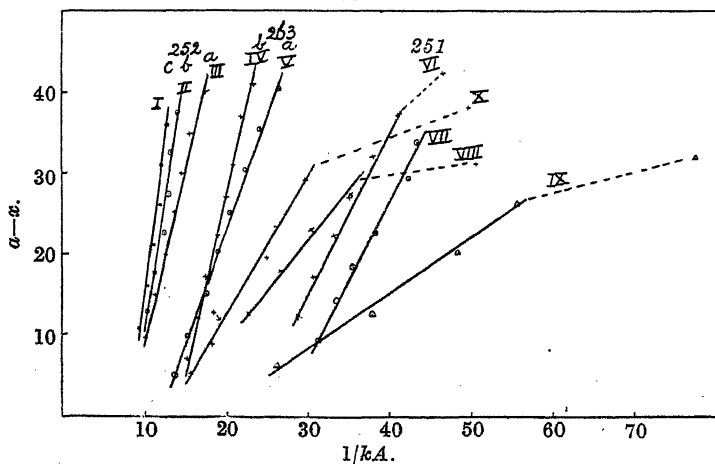
The other curves in Fig. 4 are for some experiments which were made with colloidal platinum. This was prepared by reducing platinum chloride solution with formaldehyde and dialysing. The composition of the reaction mixtures is given in Table I. The monomolecular velocity coefficients for these experiments showed a steady rise during the course of the reaction, and a very considerable deviation from the linear relation required by the Freundlich equation was found on plotting log kA against log $(a - x)$. Application of equation (4) leads to satisfactory results (Curves I—VI, Fig. 4).

Reference may be made here to Maxted's results for the poisoning of platinum catalysts by mercuric chloride (*J.*, 1922, **121**, 1760). In the decomposition of hydrogen peroxide, the poisoning of the platinum was, over a fairly wide range, proportional to the

amount of mercury salt added. On the assumption that the poisoning is due to selective adsorption of mercury, the amount of active surface thus occupied will be a measure of the poisoning action, if the decomposition of the peroxide occurs at the catalyst surface. From equation (3) the catalyst activity is proportional to the surface available for hydrogen peroxide adsorption : a linear decrease of this surface due to mercury adsorption thus corresponds to a similar decrease in activity.

The mechanism suggested in this paper may be applied to account for the varying activities shown by different substances in catalysing the decomposition of hydrogen peroxide. The activity of a surface in this respect will depend on the magnitude of its stray force fields. These will determine the extent of disturbance of the intramolecular force fields in adsorbed hydrogen peroxide molecules, and therefore the ease with which a hydrogen ion may be removed by the impact of a hydroxyl ion. The stability of hydrogen peroxide in vessels lined with paraffin wax may thus be attributed to the non-polar nature of the wax surface.

Summary.

Cobaltic hydroxide as a catalyst for the decomposition of hydrogen peroxide shows a dual change of activity; an irreversible fall, and a reversible increase varying inversely as the concentration of the peroxide.

By varying separately each factor in the reaction, it was found that (a) the apparent activity of a given mass of catalyst increases with addition of traces of ammonia to an approximately constant maximum; (b) the initial activity of the catalyst is proportional to its amount; (c) the catalyst activity is an inverse linear function of the hydrogen peroxide concentration.

A mechanism is suggested for the reaction in which the decomposition of the peroxide occurs in a monomolecular film on the catalyst surface, a distortion of the intramolecular force field on adsorption rendering one hydrogen atom of the peroxide molecule removable by the impact of a hydroxyl ion. The peroxide ion thus formed decomposes to give oxygen and hydroxyl ions. An equation derived on this basis is shown to agree with experimental data, and to be applicable to other cases of catalysis.

CLXXXII.—α-Acenaphthaquinoline.

By Jessie Stewart.

WHEN 5-aminoacenaphthene is allowed to undergo Skraup's reaction under conditions analogous to those employed by Bamberger and Stettenheimer (*Ber.*, 1891, **24**, 2474) in the preparation of α-naphthaquinoline, there results a *base* of melting point 61—62° (I). On oxidation with chromic acid it gives *α-naphthaquinoline-*6 : 7-*dicarboxylic acid* (II), which when heated with soda-lime is readily converted into α-naphthaquinoline.
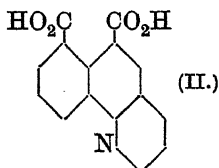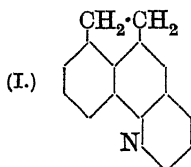
α-Acenaphthaquinoline (I).—A mixture of 10 g. of 5-aminoacenaphthene (*Ber.*, 1911, **44**, 2855), 5 g. of nitrobenzene, 18 g. of glycerol, and 8 c.c. of concentrated sulphuric acid was heated under reflux, at first very gently and finally at 150—160° for 3—4 hours. The product, while still hot, was poured into water (4 vols.). The chromate of the base (yield 10 g.), isolated exactly as in the case of α-naphthaquinoline, was decomposed by warm dilute caustic soda solution, the insoluble base washed repeatedly with water, dissolved in boiling dilute hydrochloric acid, and decolorised with animal charcoal. The hydrochloride, which crystallised, was dissolved in boiling water, decomposed with ammonia, and the base thus precipitated was extracted with ether. The extract was dried with caustic soda and allowed to evaporate, when *α-acenaphthaquinoline* crystallised in colourless needles, m. p. 61—62°, which gradually turned yellow (Found : N, 7·0. $C_{15}H_{11}N$ requires N, 6·8%).

The base is insoluble in water and very soluble in ether, alcohol, or benzene. It readily forms crystalline salts with mineral acids, these being very soluble in water, less soluble in acids, and very easily decomposed by caustic alkalis. The *picrate*,

$$C_{15}H_{11}N,C_6H_2(NO_2)_3·OH,$$
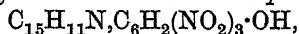
m. p. 234°, is precipitated as microscopic, yellow needles on mixing alcoholic solutions of acenaphthaquinoline and picric acid. It is insoluble in cold alcohol and difficultly soluble in boiling alcohol (Found : N, 13·1. $C_{21}H_{14}O_7N_4$ requires N, 12·9%).

*α-Naphthaquinoline-*6 : 7-*dicarboxylic Acid* (II).—An almost boiling solution of 5 g. of α-acenaphthaquinoline in 100 c.c. of glacial

acetic acid was gradually treated with 14·5 g. of powdered potassium dichromate, and the whole was boiled under reflux for about 2 hours and poured into water. The solid product, after being washed repeatedly with water, was completely extracted with hot dilute caustic soda solution, and the extract, after decolorisation with animal charcoal, was neutralised with dilute sulphuric acid. The dicarboxylic acid thus precipitated (yield 6 g.) was digested with caustic soda solution, the slightly soluble sodium salt thus formed dissolved in hot water, and the combined filtrates were boiled with charcoal. The alkaline solution was then *either* very slowly and exactly neutralised with dilute sulphuric acid—whereby the dicarboxylic acid crystallised in small, white, glistening plates—*or* made strongly acid with glacial acetic acid, whereby the dicarboxylic acid was thrown out of solution (it is not precipitated from solution by dilute acetic acid). At 150° it was completely converted into the anhydride (Found : N, 5·5, 5·8; C, 71·7; H, 2·85. $C_{15}H_7O_3N$ requires N, 5·6; C, 72·3; H, 2·8. $C_{15}H_9O_4N$ requires N, 5·2; C, 67·4; H, 3·4%).

On distillation of the acid with soda-lime, α-naphthaquinoline was obtained as a pale yellow oil which solidified immediately on inoculation. The melting point of the solid, recrystallised from light petroleum, was 49—50°, and was unchanged on admixture of α-naphthaquinoline. Its picrate, m. p. 191—192°, was identical with that of α-naphthaquinoline.

I wish to thank Mr. Holland Crompton for suggesting this work, and am continuing the investigation of the properties of the new base.

BEDFORD COLLEGE,
    UNIVERSITY OF LONDON.

CLXXXIII.—*The Solubility of Sulphur Dioxide in Water and in Aqueous Solutions of Potassium Chloride and Sodium Sulphate.*

By JOHN CHRISTOPHER HUDSON.

PREVIOUS experiments on the effect of neutral salts on the solubility of gases seem to have been chiefly concerned with the less soluble gases, such as hydrogen, oxygen and nitrogen, which, as a rule, cannot be estimated in solution by chemical means. In consequence the accuracy of the results is probably small compared with that obtainable for a more soluble gas, capable of estimation by chemical as distinct from physical methods. Further, most of the earlier

work on the subject deals with the relative effects of a large number of different salts under the same temperature conditions, rather than with the variation in the influence of any particular salt when these conditions are varied. It is therefore possible that the detailed study of the effect of a limited number of salts, as affected by wide variations of both temperature and concentration, may throw additional light on the factors involved. The importance of these considerations will be seen from the results given later for the solubility of sulphur dioxide in sodium sulphate solutions. In this case, the curve obtained by plotting solubility against salt concentration exhibits a maximum at certain temperatures; moreover, the effect of the salt (at certain concentrations) on the solubility changes sign with rising temperature. Hence an isolated determination at one temperature and concentration would give but an imperfect idea of the neutral salt effect.

It seemed desirable, therefore, to investigate the effect of neutral salts on the solubility of one of the more soluble gases over the widest possible ranges of temperature and concentration. Sulphur dioxide was chosen, partly for convenience and partly because the solubility of the gas in water itself had not yet been fully determined, the best results, due to Sims (J., 1862, 14, 1), being confined to temperatures below 60°.

Although the more soluble gases, such as sulphur dioxide and ammonia, can be estimated chemically in solution with an accuracy greater than that of the absorption methods generally used for the less soluble gases, the process of solution is probably complicated in these cases by the formation of a compound between the gas and the solvent water. Indeed, it is known from the work of Fox (Z. physikal. Chem., 1902, 41, 458), Péchard (ibid., 1900, 35, 110), and others that sulphur dioxide may combine also with the added neutral salt. Thus, whereas the effect of a second solute on the solubility of the less soluble and neutral gases, where a diminution in solubility is generally observed, may be ascribed to hydration of the neutral salt, the solubility of the more soluble and reactive gases is probably determined by two main factors : compound formation, which tends to increase the solubility, and hydration of the added salt, which has the opposite effect.

The experimental work described in this paper includes a determination of the solubility of sulphur dioxide :

(1) in water between 10° and 90°,

(2) in aqueous solutions of potassium chloride, containing up to 30 g. of salt per 100 g. of water, also between 10° and 90°,

(3) in aqueous solutions of sodium sulphate, containing up to 20 g. of salt per 100 g. of water, between 20° and 50°.

.The lower temperature limit (10°) is imposed by the fact that below 7° a saturated solution of sulphur dioxide is supersaturated with respect to the crystalline hydrate $SO_2,7H_2O$ (Roozeboom, *Rec. trav. chim.*, 1884, **3**, 46). On the other hand, experimental difficulties increase rapidly as the temperature rises and it was not found possible to make reasonably accurate determinations above 90°.

<center>EXPERIMENTAL.</center>

The experimental method adopted consisted in bubbling the gas through the solutions under investigation until they were saturated and then analysing them. The essential requirements of such a method include :

1. The direct measurement of the total pressure over the solution, from which the partial pressure of the gas may be calculated.
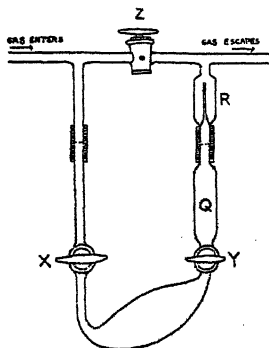
<center>FIG. 1.   FIG. 3.</center>
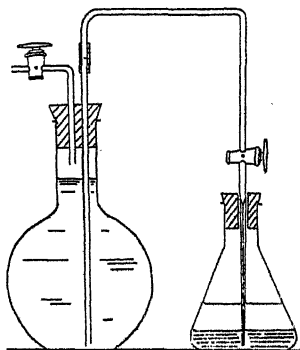
2. The complete displacement of all inert gases from the apparatus.

3. A method of sampling which does not involve a change in pressure over the solution.

4. The analysis of a sample which consists entirely of the liquid phase, so that no corrections are necessary for quantities of gas not actually dissolved.

5. An accurate method of analysis.

6. A check on the accuracy of the results by approaching the equilibrium from both sides.

Failure to comply with one or more of these conditions has proved the weak point in previous experimental methods. For instance, a method of sampling which involves suction into a pipette cannot be expected to yield accurate results in the case of sulphur dioxide, as Lindner (*Ber. K. Akad. Wiss. Wien*, 1912, **121**, 293) remarks.

In the saturator finally adopted, the absorption bulb had a capacity of about 35 c.c. and was blown in such a form as to minimise

the head of solution through which the gas was bubbled (Fig. 1). The bulb was closed by two glass taps, X and Y. It was charged with the liquid under investigation, attached by pieces of pressure tubing to the two limbs of a double T-piece, Z, and placed in a thermostat at the required temperature. The ends of the T-piece were then connected with the gas supply and the manometers, as shown in Fig. 2.

S is a siphon of sulphur dioxide. The purity of siphon sulphur dioxide is known to be high, the chief impurity being water, which seldom exceeds 0·4%. Most of the solutions were analysed after saturation and, in these cases, the presence of water in the gas would not affect the results.

FIG. 2.
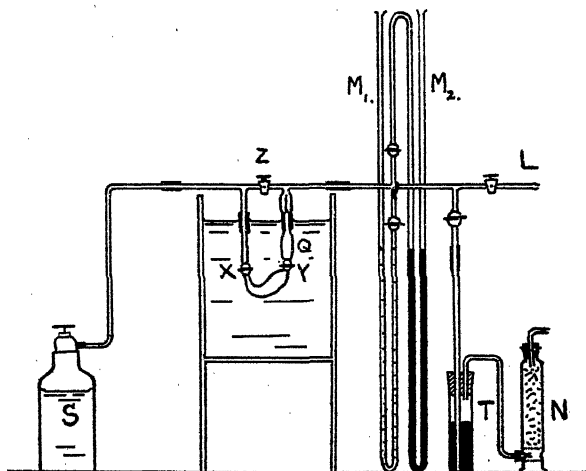
M_1 and M_2 are oil and mercury manometers respectively. The oil used was a light mineral oil of d 0·870. It absorbed sulphur dioxide, but this did not alter its density to an appreciable extent. T is a bottle containing mercury, which serves to regulate the internal pressure. N is a soda-lime tower for absorbing the excess of gas.

The necessary connexions were made by small pieces of pressure tubing.

When the bulb had acquired the temperature of the bath, the apparatus was evacuated by a water-pump connected to L. Sulphur dioxide was admitted from the siphon and allowed to bubble out through T. This evacuation and sweeping out with the gas was repeated several times, so that air was completely expelled from the apparatus. When the tap Z was closed, the gas bubbled through the solution, the excess of liquid being displaced into the small bulb Q. The bubbling was continued until saturation was completed.

Half an hour was usually sufficient, but most experiments were continued for much longer periods, with a minimum of 1 hour. Tap Z was then opened; the solution flowed back into the bulb and filled it, whereupon taps X and Y were closed under water.   At temperatures above 60°, owing to the running of the lubricant on the taps, it was found advisable to carry out the saturation with the taps X and Y just outside the bath.   In these cases the bulb was not completely filled with solution and a small correction was therefore made for this fact.

The tube and its contents, after being disconnected and dried externally, was weighed, any solution left in Q having been removed with the help of filter-paper.

Determinations of the solubility reached from the side of supersaturation were made by passing the gas for an hour or so at a lower temperature or under a greater pressure than the equilibrium values, and then continuing the bubbling for another 3 hours at the final temperature and pressure before analysing the solution.

The analytical methods used varied with the nature of the solution.

1. *Water and Potassium Chloride Solutions.*—The sample was transferred to a conical flask as follows : About 200 c.c. of water containing some caustic soda and hydrogen peroxide were placed in the flask, which was closed by a rubber stopper.   Two glass tubes passed through the latter, one of these was straight and vertical and dipped below the liquid in the flask, the other was a short piece bent at right angles.   The bulb containing the sample was inverted and the end Q (Fig. 1) was attached to the long vertical tube by means of a small piece of pressure tubing.   The other limb of the bulb was dipped under a further quantity of dilute alkali and hydrogen peroxide contained in a small beaker.   When suction was applied through the small bent glass-tube and taps X and Y were opened, the sample was swept out into the conical flask without any loss.   The total quantities of caustic soda and of hydrogen peroxide used were in slight excess of those necessary to convert the sulphurous acid completely into sodium sulphate.*

The resulting solution was heated on the steam-bath to destroy the excess of hydrogen peroxide, cooled, and diluted to 1 litre. Measured portions were then taken for the determination (in duplicate) of sulphate as barium sulphate, and of chloride as silver chloride, when necessary.

2. *Sodium Sulphate Solutions.*—As the presence of sulphate interferes with the gravimetric determinations in the case of sodium sulphate solutions, it was more convenient to estimate the dissolved sulphur dioxide volumetrically.   A large number of experiments

* Analytical reagents were used.

were made on the iodimetric titration of sulphurous acid which confirmed the conclusion of Raschig (*Z. anorg. Chem.*, 1904, **17**, 577) and Macaulay (J., 1922, **121**, 553) that the low results frequently obtained in this estimation are due almost entirely to the escape of sulphur dioxide from the solutions; *e.g.*, a 0·05*N*-sulphurous acid solution, stored in a litre flask and communicating with the atmosphere only through a narrow glass tube, lost more than 1% of its strength in 40 minutes.

In order to minimise losses of sulphur dioxide, the solution obtained from the saturator was transferred to a flask of water of about 1 litre capacity so that it filled the latter almost completely. The flask, containing the diluted sulphurous acid solution, was weighed and was then fitted with a siphon ending in a glass tap and capillary jet (Fig. 3). The iodine solution was stored in a large stock bottle of the type recommended by Rice, Kilpatrick, and Lemkin (*J. Amer. Chem. Soc.*, 1923, **45**, 1361), which was also fitted with a glass tap and capillary jet. About 70 c.c. of water were introduced into a small conical flask, followed by about 30 g. of iodine solution, the flask and contents being weighed before and after the introduction of the iodine. The weight of solution removed on the tip of the capillary tube was found to be negligible. When the iodine was run in slowly, it formed a distinct layer under the water so that loss of iodine was reduced considerably. The sulphurous acid was then run in until the colour of the iodine was discharged and a third weighing gave the weight of sulphurous acid. The final endpoint was obtained by the addition of starch and small quantities of a very dilute iodine solution until the solution assumed a standard tint.

Three titrations were made and approximately 80 c.c. of the sulphurous acid were used altogether, so that the volume of the gaseous phase over the solution of sulphur dioxide in the flask seldom exceeded 150 c.c. and was often less. Consequently, the maximum loss arising from evaporation of the sulphur dioxide into the gaseous space above the solution, on the assumption that all the gas was originally in the solution, that no diffusion occurs into the atmosphere, and that there is no oxidation,* should not exceed 0·4%.

The following results for a given sulphurous acid solution serve to show the accuracy which may be obtained by this method :

Wt. of iodine soln. (g.)	19·705	22·085	19·755
Wt. of sulphurous acid soln. (g.)	26·495	29·71	26·60
Ratio	0·7437	0·7434	0·7427

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* Atmospheric oxidation of dilute sulphurous acid solutions is almost negligible over short periods. Thus experiments showed that several hours elapsed before such solutions, exposed to the air in test-tubes, gave any turbidity with barium chloride in dilute hydrochloric acid.

The iodine solutions employed were standardised against anhydrous sodium thiosulphate (see Young, *J. Amer. Chem. Soc.*, 1904, **26**, 1028).

The procedure for the titration of iodine by sulphurous acid described above was found to double the accuracy of the method. The maximum difference between any two titrations of the same solution amounted to 0·43% (mean from 26 series) as against 0·88% for the ordinary volumetric method (12 series). Further, the new method gave results in good agreement with the gravimetric values. It was found, again in agreement with Macaulay, that, if rigorous precautions are taken to prevent volatilisation, it is immaterial whether the sulphurous acid solution is added to the iodine (A) or *vice versa* (B); the iodine solution was *ca.* 0·09(weight)N :

<div align="center">

Ratio I_2/SO_2 *by Weight.*

</div>

A	0·7071	0·7050	0·7062	Mean 0·7061
B	0·7070	0·7043	0·7048	Mean 0·7054

The solutions of sodium sulphate were prepared directly by weight from the analytically pure salt. Concentration changes due to evaporation of the water whilst the gas was bubbling through the solution were minimised by previously passing the gas through a solution of approximately the same composition as that being saturated. As a check, the tubes and contents were weighed before and after saturation. The observed increase in weight was usually equal to the amount of sulphur dioxide found by analysis.

Temperature	20°	30°	40°	50°	50°	60°
Increase in weight...	3·31	2·52	1·80	1·51	1·64	1·23 g.
SO_2 found	3·28	2·55	1·84	1·52	1·64	1·40 ,,
Difference	0·03	0·03	0·04	0·01	—	0·17 ,,

As the weight of water in the sample was about 30 g. and the sulphur dioxide was actually estimated in the solutions, these small differences, which affect the water only, are within the limits of experimental error between 20° and 50°. Above 50°, the loss of water by evaporation is much greater and there is correspondingly less certainty that the final concentration of the salt is equal to its initial value.

Calculation of Results.—In order to illustrate the method of calculation, a typical experiment will be described in detail.

The lowering of the vapour pressure of water by both the dissolved gas and the added neutral salt has been assumed equal to the sum of the depressions which would have been caused by each solute separately. The lowering of the vapour pressure due to the sulphur dioxide was calculated by Raoult's law on the assumption that water is bimolecular. The correction is not great, ranging

from 0·1% at 10° to 1·25% at 90°. These figures are probably less than the experimental errors at these temperatures.* On the other hand, the correction for dissolved salt is considerable, rising in the case of potassium chloride to approximately 75 mm. at 90° for a solution containing 30 g. of salt per 100 g. of water. The values were calculated from Tammann's data (*Wied. Ann.*, 1885, **24**, 530).

The foregoing corrections are only approximate, as there are grounds for believing that sulphur dioxide combines both with the water and with the added salts, and, therefore, neither Raoult's law nor the empirical formula deduced from Tammann's data can be regarded as strictly applicable. Nevertheless, some such correction is essential and the mode of attack adopted seems the only one available at present. In order that others may be able to correlate their results with the present values, the total pressure actually measured over the solution is given for the experiments in water and potassium chloride solutions without any correction other than that for the temperature of the barometer.

Experiment 99.   At 90°.

Internal volume of the bulb as determined by calibration with water, 42.8 c.c.

Sample : wt. 38·46 g.; d 1·17. Therefore volume, 32·9 c.c.

Vol. of gas, 42·8—32·9 = 9·9 c.c.

Wt. of $BaSO_4$, 0·3909, 0·3902 g. (250 c.c. for analysis.) Therefore total SO_2, 0·4287 g.

Wt. of AgCl, 0·8690, 0·8697 (49·92 c.c. for analysis). Therefore wt. of KCl, 9·385 g.

Wt. of water in the sample = 38·46 — 0·429 — 9·385 = 28·65 g.

G. of KCl per 100 g. of water = 9·385 ÷ 0·2865 = 32·75.

Barometer, 764·0 mm. Mercury manometer, 205 mm. Temperature correction, 3·4 mm.

Vapour pressure of water at 90°, 525·9 mm.

Calc. lowering of the vapour pressure : (*a*) By SO_2, 5·2 mm.; (*b*) By KCl, 75·5 mm. Therefore corrected vapour pressure, 525·9 — 5·2 — 75·5 = 445·2 mm.

Partial pressure of the sulphur dioxide over the solution, 764·0 + 205 — 3·4 — 445·2 = 520 mm.

Wt. of 9·9 c.c. of SO_2 at 90° and 520 mm., 0·0145 g.† Therefore SO_2 dissolved, 0·4287 — 0·0145 = 0·4142 g.

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* Even if Kendall's contention (*J. Amer. Chem. Soc.*, 1921, **42**, 1391) that, in such calculations, the molecular weight of water should be taken as 18, is accepted, the differences involved have no significance in the present case.

† The weight of water vapour contained in the gaseous space is negligible.

Solubility, assuming Henry's law, $\dfrac{0.4142 \times 760 \times 100}{520 \times 28.65} = 2.113$ g. of SO_2 per 100 g. of water, containing 32.75 g. of potassium chloride.

The experimental results are recorded in the following tables and figures : $P =$ total pressure. $p =$ partial pressure of sulphur dioxide. $S_1 =$ g. of sulphur dioxide per 100 g. of water. $y =$ g. of potassium chloride per 100 g. of water. $z =$ g. of sodium sulphate per 100 g. of water. The solubility $(S_0$ or $S) = S_1 \times 760/p$, the weight of sulphur dioxide dissolved per 100 g. of water, the partial pressure of the gas over the solution being 760 mm. of mercury.

TABLE I.

The Solubility of Sulphur Dioxide in Water (See also Fig. 4).

$P.$	$p.$	$S_1.$	$S_0.$	$P.$	$p.$	$S_1.$	$S_0.$
	Temp. 10°.				Temp. 48.15°.		
777.3	764.2	15.53	15.44	799.0	717.0	4.147	4.395*
776.3	767.1	15.50	15.36	801.5	719.5	4.132	4.365
776.2	767.0	15.58	15.44	794.3	712.3	4.108	4.382
775.4	766.2	15.48	15.36	840.9	758.9	4.409	4.415
766.2	757.0	15.28	15.32*			Mean 4.39	
		Mean 15.39					
	Temp. 15°.				Temp. 60°.		
769.5	757.6	12.72	12.76	881.5	735	3.151	3.257
772.5	760.6	12.75	12.74	894.5	748	3.192	3.244
769.5	757.6	12.64	12.68	894.5	748	3.215	3.268
		Mean 12.73		886.5	740	3.142	3.220*
						Mean 3.25	
	Temp. 20°.				Temp. 70°.		
787.7	771.3	10.79	10.63	897	666.5	2.278	2.598
773.3	765.9	10.61	10.66	892.5	662	2.277	2.614
778.6	762.2	10.68	10.64	893	662.5	2.300	2.637*
779.1	762.7	10.65	10.61	892	661.5	2.251	2.585*
773.9	757.5	10.64	10.68*			Mean 2.61	
		Mean 10.64					
	Temp. 29.9°.				Temp. 80°.		
798.5	768.5	7.640	7.554*	883	531.5	1.496	2.139
789.4	759.4	7.600	7.607	883	531.5	1.490	2.131
791.0	761.0	7.610	7.600*	958	606.5	1.704	2.130*
800.9	770.9	7.674	7.565	967	616	1.714	2.114*
		Mean 7.58				Mean 2.13	
	Temp. 40°.				Temp. 90°.		
800.9	747.3	5.428	5.520	893	378	0.901	1.801
801.4	747.8	5.441	5.529*	954.3	439.5	1.037	1.785
798.1	744.5	5.406	5.516	960	439	1.056	1.829
816.7	763.1	5.593	5.569			Mean 1.805	
815.7	762.1	5.585	5.555*				
815.7	762.1	5.581	5.550*				
		Mean 5.54					

* denotes a supersaturation experiment.

TABLE II.

The Solubility of Sulphur Dioxide in Potassium Chloride Solutions
(See also Fig. 5).

P	p	y	S_1	S	P	p	y	S_1	S
Temp. 10°:					*Temp. 48·15°.*				
		0		15·39			θ		4·39
780·3	772·0	5·55	17·32	17·05	841·8	761·7	5·06	4·712	4·70
780·3	772·2	10·22	18·88	18·58	841·8	763·6	10·14	4·968	4·945
766·2	758·3	15·85	20·23	20·28*	826·9	750·7	15·82	5·180	5·24
766·2	758·4	20·78	21·92	21·96*	839·8	765·7	21·11	5·521	5·48
768·2	761·4	29·90	25·45	25·40	826·9	754·0	25·09	5·703	5·74
					839·8	769·7	32·72	6·258	6·18
Temp. 15°.					*Temp. 60°.*				
		0		12·66			0		3·25
772·2	760·8	10·39	15·30	15·32	889	746	5·30	3·384	3·45
771·9	761·0	19·91	17·67	17·64	888	748	10·67	3·468	3·52
772·2	761·9	30·71	20·64	20·59	896	763·5	21·12	3·943	3·92
					890·5	764	30·98	4·258	4·24
Temp. 20°.					*Temp. 70°.*				
		0		10·64			0		2·61
773·9	757·9	5·14	11·60	11·62*	969	747·5	8·74	2·756	2·80
774·6	758·9	10·30	12·50	12·52	960·5	752	21·68	3·016	3·05
778·0	761·7	15·61	13·58	13·55	960	757	30·73	3·251	3·26
774·0	759·4	24·98	15·37	15·38					
779·0	764·8	30·38	16·76	16·65*					
Temp. 29·9°.					*Temp. 80°.*				
		0		7·58			0		2·13
788·6	759·3	5·19	8·204	8·21	958	620	8·66	1·850	2·27
789·4	760·7	10·11	8·810	8·80	961	643	21·35	2·043	2·415
784·0	756·7	20·82	10·00	10·05	961	656	29·68	2·179	2·52
782·8	756·8	29·86	11·21	11·26					
Temp. 40°.					*Temp. 90°.*				
		0		5·54			0		1·81
816·7	764·3	5·17	5·994	5·96	967·5	468	9·23	1·142	1·855
818·1	766·9	10·20	6·380	6·32	958	482	19·49	1·248	1·97
810·4	759·2	10·40	6·380	6·39*	965·5	520	32·75	1·445	2·11
818·1	768·1	15·44	6·869	6·675					
810·4	761·6	20·14	7·086	7·07*					
803·7	756·0	24·83	7·415	7·45					
803·7	757·0	28·95	7·721	7·75					

* denotes a supersaturation experiment.

TABLE III.

The Solubility of Sulphur Dioxide in Sodium Sulphate Solutions
(See also Fig. 6).

Temp. 20°

z	0	1·94	4·93	7·95	10·00	15·00	20·00
S_1	10·64	10·66	10·57	10·36	10·07	9·66	9·17

Temp. 30°

z	0	2·04	3·99	5·47	7·83	10·00	20·01
S_1	7·608	7·709	7·776	7·773	7·716	7·586	7·006

Temp. 40°

z	0	2·49	5·04	7·95	10·00	14·94	20·01
S_1	5·585	5·812	5·910	5·927	5·882	5·802	5·630

Temp. 50°

z	0	2·49	5·04	10·04	14·94	19·99
S_1	4·214	4·508	4·678	4·728	4·730	4·648

Details of the total and partial pressures have been omitted in Table III because, except in three cases, the calculated value of the partial pressure of the gas over the solution was within 10 mm. of 760 mm. The results were corrected to 760 mm. on the basis of Henry's law.

Discussion of Results.

A. *Solubility in Water.*—The solubility of sulphur dioxide in water was first determined by Schönfeld (*Annalen*, 1855, **95**, 1).

FIG. 4.

The solubility of SO$_2$ in water.   (Under a partial pressure of 760 mm. Hg).
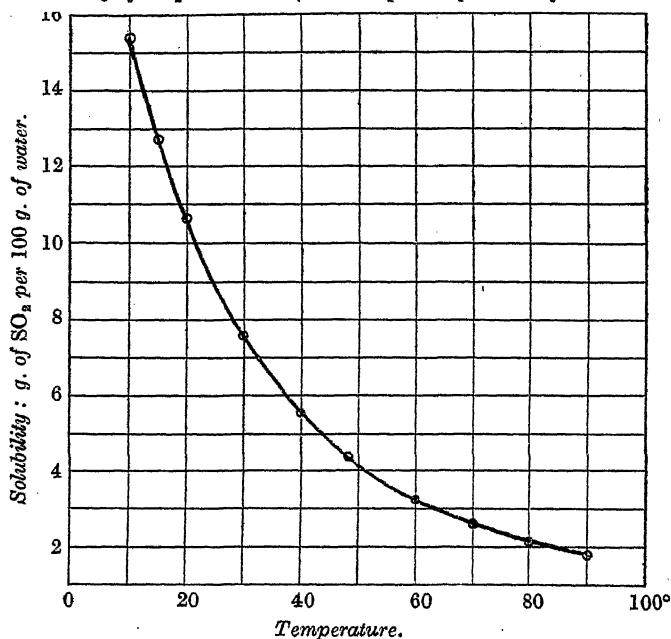
The results obtained—quoted to five significant figures—are the only ones given in the most recent edition of Landolt and Börnstein's Tables.

Apart from grave sources of error in this work, such as failure to correct for the vapour pressure of water, erroneous values for the densities of the solutions (see Roozeboom, *Rec. trav. chim.*, 1884, **3**, 57), and the doubtful accuracy of the method of analysis, it should be noted that the solubilities given in Landolt and Börnstein's Tables are calculated from two quadratic formulæ deduced by Schönfeld. Since, however, the percentage differences between the calculated and the observed values for Schönfeld's nine experi-

mental points are $-1\cdot1$, $+2\cdot7$, $-0\cdot6$, $-2\cdot2$, $+4\cdot0$, $-1\cdot0$, $-2\cdot5$, $+5\cdot5$, $-2\cdot1$, it appears that the five significant figures given in the Tables have little meaning.

It is surprising that the results obtained by Sims (J., 1862, **14**, 1) should have been overlooked. The results obtained in the present investigation agree well with his values, although somewhat lower figures are obtained at the higher temperatures in agreement with Smith and Parkhurst (*J. Amer. Chem. Soc.*, 1922, **44**, 1918), who state that their results are consistently below those of Sims. These American investigators were chiefly concerned with the solubility of sulphur dioxide in suspensions of calcium and magnesium hydroxides, and the number of actual experimental determinations of the solubility in water itself reported in their paper is small. Their values for the solubility are recorded in the comparative table below. The agreement is good, save at 60°, but it should be noted that the solubility value at this temperature quoted for Smith and Parkhurst is based on the figure obtained with a partial pressure of sulphur dioxide of only 175·7 mm. The necessary extrapolation, based on Henry's law, to the standard pressure of 760 mm. gives a value 3·63 as against 3·25 obtained in the present investigation, but, as shown by Sims and Lindner, this extrapolation will undoubtedly give too high values of the solubility. Lindner (*Ber. K. Akad. Wiss. Wien*, 1912, **121**, 293) explained the deviations from Henry's law on the hypothesis that the ratio of the concentrations of the free sulphur dioxide molecules, as distinct from the ionised sulphurous acid, was constant for the two phases and, using Sim's data, he obtained results in good quantitative agreement with this suggestion. He was less fortunate, however, with results which he obtained himself. He made only four experiments; the value quoted below for 50° is extrapolated from a measurement at 700 mm. In his other experiments, the partial pressure of the gas was small compared with one atmosphere, so that accurate extrapolation is not possible.

In the present series of experiments, errors due to deviation from Henry's law were reduced to a minimum at all temperatures up to 60° by arranging that the partial pressure of the gas should be as nearly atmospheric as possible. This was done by adjusting the height of the mercury in the bottle T (Fig. 2). Owing to the rapid rise in the vapour pressure of water, it was not possible to do this at higher temperatures, since the glass taps would not withstand considerable internal pressures. On the other hand, there is less objection to the application of Henry's law at higher temperatures.

A comparative table of the results of various investigations is given below.

Solubility of Sulphur Dioxide in Water.

	Schönfeld.	Sims.	Smith and Parkhurst.	Lindner.	Hudson.
10°	16·21	15·4			15·39
15	13·54	12·55			12·73
20	11·28	10·4	10·81		10·64
25	9·41	8·95			8·98
30	7·80	7·8			7·56
40	5·41	5·8	5·52		5·54
50		4·5		3·95	4·14
60			3·63		3·25

The values for the solubility given above are expressed as g. of sulphur dioxide per 100 g. of water when the partial pressure of the gas is 760 mm. of mercury, with the following exceptions:

1. Schönfeld's results refer to a *total* pressure of 760 mm.

2. Smith and Parkhurst, and Lindner gave their results in terms of 100 c.c. of water.

B. Solubility in Salt Solutions.—It will be seen from Fig. 5, in which the solubility of sulphur dioxide is plotted against the concentration of potassium chloride, that the curves ôbtained are very nearly straight lines at all temperatures, in agreement with the results of Fox (*loc. cit.*) for this salt at 25° and 35°. If S is the solubility of the gas in a solution containing y grams of potassium chloride per 100 grams of water, then the formula $S = S_0 + ay$ represents the results with considerable accuracy. The most probable values of the constants S_0 and a (calculated by the method of mean squares) are given in the following table, together with the corresponding values of the relative increase in solubility, which may conveniently be taken as the percentage increase in the solubility per gram of salt added, and which is given by

$$k = \frac{S - S_0}{S_0} \cdot \frac{100}{y} = \frac{100a}{S_0}.$$

Temp.	S_0.	a.	k.	Temp.	S_0.	a.	k.
10°	15·21	0·3328	2·187	48·15°	4·399	0·05352	1·217
15	12·66	0·2534	2·017	60	3·267	0·03007	0·920
20	10·57	0·1958	1·852	70	2·615	0·02059	0·787
29·9	7·567	0·1223	1·616	80	2·142	0·01294	0·604
40	5·557	0·07565	1·361	90	1·793	0·00939	0·524

The values of S_0 obtained in this way are generally in good agreement with the experimental values for the solubility of sulphur dioxide in water, as tabulated on page 1340. At 10° and 15°, however, the differences between the observed and the calculated values of S_0 are somewhat greater, corresponding probably with a slight departure from the linear relationship at these temperatures.

The results for the solubility of sulphur dioxide in sodium sulphate

solutions are rather surprising. At 30°, 40°, and 50°, the solubility–salt concentration curves exhibit distinct maxima, as shown in Fig. 6. There is probably a maximum solubility at 20° also.

FIG. 5.

The solubility of sulphur dioxide in aqueous solutions of potassium chloride.
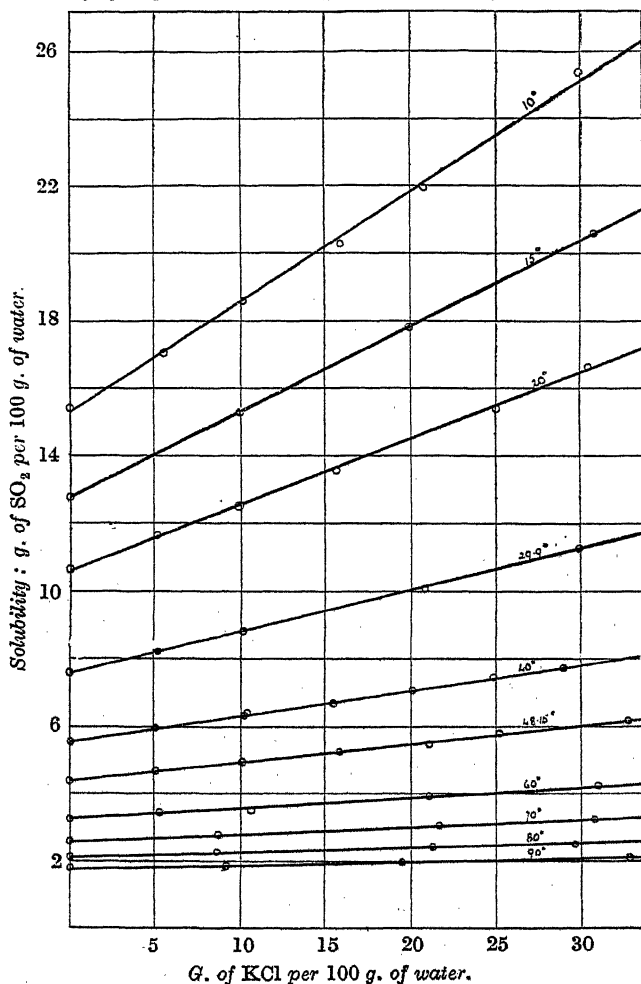
The actual position of the maximum is difficult to determine, but it is clear that it moves to the left with falling temperature. A few experiments at 10°, not reported here, render it possible that the maximum may disappear altogether at this temperature, but further experimental evidence is necessary to establish this point.

z z* 2

Fox (*loc. cit.*) investigated the solubility of sulphur dioxide in a large number of salt solutions at 25° and 35°. It is rather difficult to correlate his results with the present values, as he expressed them in terms of the solubility coefficient, and, in order to effect a comparison, a knowledge of the densities of the various solutions would be necessary. The values for the densities of solutions of the salts alone are not sufficient, for, at these temperatures, considerable expansion of the solutions occurs when the sulphur dioxide dissolves. In the case of sodium sulphate, Fox observed a diminution in

FIG. 6.

G. of Na_2SO_4 *per 100 g. of water.*
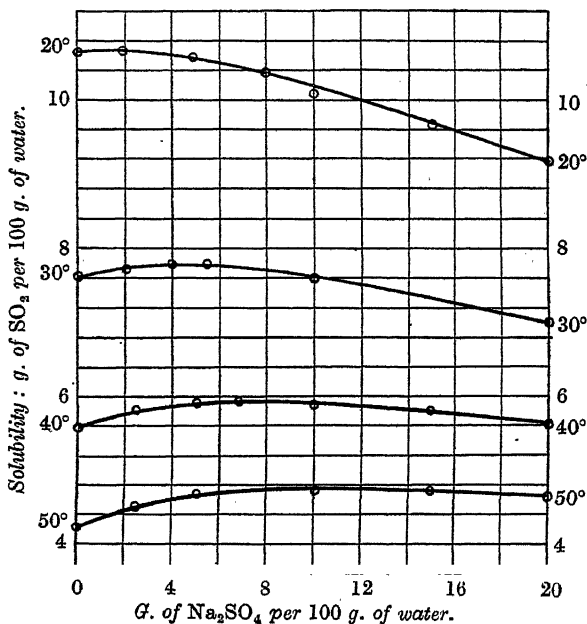
The solubility of sulphur dioxide in sodium sulphate solutions.

solubility following a linear law at both temperatures. The necessary corrections for the densities of the respective solutions might conceivably reverse the sign of the effects observed by him, but it is difficult to see how this would account for the occurrence of maximum values. The difficulty of correlation is further increased by the fact that Fox does not appear to have measured the pressures over his solutions.

As suggested on page 1334, the two main factors determining the solubility of sulphur dioxide in salt solutions are probably the hydration of the salt and the tendency to combination between the salt and the gas. It might be possible, on the basis of the hydration

values for salts already on record, to attempt an estimate of the significance of these two factors, but it is felt that such an attempt should be postponed until a much larger mass of experimental data for the influence of neutral salts on the solubility of this gas over a wide temperature range is available.

In conclusion, the author desires to express his thanks to Professor J. C. Philip, F.R.S., who suggested this research, for the valuable assistance and criticism which he has generously given throughout the course of the work. The author is indebted also to Dr. H. F. Harwood for advice concerning the methods of analysis, and to the Department of Scientific and Industrial Research for a grant which has rendered it possible for him to undertake this investigation.

CLXXXIV.—*Low Temperature Oxidation at Charcoal Surfaces. Part I. The Behaviour of Charcoal in the absence of Promoters.*

By ERIC KEIGHTLEY RIDEAL and WINIFRED MARY WRIGHT.

THE results of numerous investigations on the adsorption of oxygen by charcoal, notably by Baker (J., 1889, **51**, 249), Dewar (*Compt. rend.*, 1904, **139**, 201), Rhead and Wheeler (J., 1913, **103**, 461, 1210), and Hulett (*J. Amer. Chem. Soc.*, 1920, **42**, 1408), indicate that oxygen may be adsorbed on a charcoal surface to form at least three types of surface compounds*; one removable only as oxides of carbon at extremely high temperatures (*ca.* 1000°), another removable as oxides of carbon by evacuation or by fusion with sodium carbonate (Taylor, *J. Amer. Chem. Soc.*, 1921, **43**, 2059), and a third, formed in larger quantities by adsorption at low temperatures, which can be recovered as oxygen (Dewar and Hulett).

The last form of adsorbed oxygen is endowed with catalytic properties, for not only does low-temperature autoxidation of the charcoal with liberation of carbon dioxide occur, but many oxidative processes may be catalytically accelerated by charcoal. Thus, Calvert (J., 1867, **20**, 293) noted the oxidation of ethyl alcohol vapour and gaseous hydrocarbons, recently confirmed by Firth (*Trans. Faraday Soc.*, 1924, **20**, 370). Feigel (*Z. anorg. Chem.*, 1921, **119**, 305) noted the catalytic oxidation of solutions of sulphides,

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* Professor Armstrong has pointed out that there exist three forms of carbon in charcoal, *viz.*, diamond, paraffin, and ethenoid (to which the colour is due).

chromates and iodides. The investigations of Warburg and his co-workers on the catalytic oxidation of oxalic acid and certain α-amino-acids (*Pflüg. Arch.*, 1914, **155**, 547; *Biochem. Z.*, 1921, **113**, 257), of Meyerhof on the oxidation of glucose in the presence of phosphoric acid (*Biochem. Z.*, 1923, **135**, 558) are the most complete in this respect.

Warburg (*ibid.*, 1924, **145**, 461) has shown that the property of charcoals of adsorbing solutes from aqueous solution is not con-nected with their catalytic powers, and suggested, somewhat vaguely, a differentiation of the charcoal surface into two modific-ations, both of which adsorb solutes but only one is catalytically active. He showed that sugar charcoal does not owe its catalytic properties to iron, although iron in certain forms is a very definite promoter. The results of the determinations of the velocity coefficients of the reactions by Freundlich, Warburg, and Negelein may be summarised as follows :—

(1) The reaction velocity varies inversely as the concentration of the solute, in the case of oxalic acid.

(2) The reaction velocity varies as the square root of the oxygen pressure, in the case of phenylthiocarbamide.

(3) The temperature coefficients for the oxidation of oxalic acid and cystine on blood charcoal are 2·1 and 2·3 respectively.

Freundlich and Bjerke (*Z. physikal. Chem.*, 1916, **91**, 31) con-sidered that the mechanism of the oxidation of phenylthiocarbamide consisted in the adsorption of a film of the substance on the surface of charcoal, the film thickness varying as the bulk concentration of the solute. The oxygen had to diffuse through this film for reaction, and the diffusion rate was assumed to vary as the square root of the gas pressure.

The experimental results of Warburg for cystine, however, do not agree well with the square-root relationship of Freundlich for phenyl-thiocarbamide. Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1361), in discussing his theory of the unimolecular nature of the adsorbed film, suggested that the oxygen molecule on striking a charcoal surface would occupy two elementary spaces on the lattice, and that the oxygen atom on each space would take part in the reaction; the concentration of oxygen atoms on the surface could then be regarded as proportional to the square root of the oxygen pressure.

That a difference in properties of various parts of a clean catalyst-surface must exist, has long been known, and can readily be deduced from a consideration of the various physical modifications of the material which exist on the surface, *e.g.*, crystal facets, edges, and partly isolated atoms, each form possessing different surface energy. From the effect of minute traces of poisons on the catalytic activity,

also, although less conclusively, from the variation in the magnitudes of the saturation maximum of adsorption of various gases, similar conclusions as to the existence of areas of different activity on a surface may be drawn. The first quantitative attempt to determine the area of the catalytically active portion of a solid catalyst was made by one of us (Rideal, J., 1922, **121**, 309) in an examination of the catalytic efficiency of a nickel surface for the combination of ethylene and hydrogen. The work of Pease (*J. Amer. Chem. Soc.*, 1923, **45**, 1196) on quantitative poisoning provides data for similar calculations on a copper surface; whilst in solutions the question of fractional poisoning has been investigated by Maxted (J., 1922, **121**, 1760) and by Vavon and Husson (*Compt. rend.*, 1922, **175**, 277). In the case of charcoal, it is to be anticipated, on this conception of a variability of surface activity, that the existence of different forms of surface should be capable of experimental demonstration. A number of carbon atoms in the surface may be regarded as being readily detachable, being held less tenaciously than atoms in the regular space lattice, and should readily react with oxygen and be disengaged as carbon dioxide, and constitute the autoxidisable fraction. There exists in addition a fraction of the surface on which oxygen is strongly adsorbed, but from which carbon dioxide can be evolved only at high temperatures; this composite surface is very stable, and adsorbed molecules on it either evaporate unchanged or remain as a compound on the surface, no catalytic action taking place. Thus diamond facets adsorb dyes with facility, but do not promote catalytic oxidation. In addition to these two extremes, there exists a portion of the surface from which carbon dioxide may be evolved at comparatively low temperatures; this oxygen complex apparently passes over to the more stable form with time. The union of the carbon atoms with the underlying solid is in this case less strong than in the former but stronger than for the autoxidisable surface, and the adsorbed reactant oxygen on excitation is capable either of entering into a more complete combination with the underlying carbon or of oxidising a molecule of an oxidisable reactant adsorbed in juxtaposition to it.

The data on the heat of adsorption of oxygen by charcoal (Blench and Garner, J., 1924, **125**, 1288) provide additional support for such an assumption, for they found that the heat of adsorption is in part greater than the heat of oxidation of carbon. Since the energy of oxidation of carbon involves the endothermic breaking of carbon linkings, Garner's data indicate that on the surface of carbon some of the linkings in the carbon skeleton are already broken. These atoms are less saturated than those completing a graphite ring, and we should anticipate that they would possess a greater chemical

reactivity. An attempt has now been made to measure the areas of these different surfaces on the charcoal, and the effects of variation in oxygen pressure and in concentration of acid on the rate of oxidation on the surface have been investigated.

EXPERIMENTAL.

A. Autoxidation.

Kahlbaum's sugar charcoal was washed in silica vessels with boiling conductivity water to remove soluble impurities and dried by heating in a platinum dish; one portion was activated by heating in silica vessels by Millar's method (*J. Amer. Chem. Soc.*, 1922, 44, 1866), another by heating in a stream of hydrogen. The resulting charcoals were equally active, and retained their activity when preserved from contamination, or exposure to the laboratory air.

The charcoal contained 1·1% of ash, chiefly silica, calcium, potash, and a trace of iron (0·8% of the ash). The mean diameter of the charcoal particles was 0·4μ (average of 200 counts).

The rate of autoxidation of this charcoal was determined by measuring the rate of oxygen uptake, from air and from oxygen, and of evolution of carbon dioxide, from 100 mg. of charcoal suspended in 3 c.c of conductivity water in a shaking apparatus with a Barcroft differential manometer (*Biochem. Z.*, 1917, 81, 319). In one set of experiments, the carbon dioxide was absorbed in a 40% solution of potash, so that the pressure change was proportional to the oxygen-uptake. In another series, no potash was used, so that the pressure change was proportional to the difference in the amounts of the carbon dioxide evolved and the oxygen taken up. There is a small error due to the carbon dioxide adsorbed by the charcoal and that dissolved in the water, but after about 4 hours the amount adsorbed is negligible compared with that evolved.

The reaction velocity after preliminary agitation of the mixture for $\frac{1}{2}$ hour conformed to a reaction of zero order, and for every molecule of oxygen adsorbed an equivalent of carbon dioxide was evolved.

The oxygen uptake is given in the following table, also the velocity coefficient k, calculated in cubic mm. of oxygen per hour (N.T.P.) per mg. of charcoal.

From these data the temperature coefficient is found to be $k_{50°}/k_{40°} = 1·8$. Also the rate of autoxidation is independent of the oxygen pressure over the range of pressures examined.

As has been indicated, we should anticipate autoxidation to occur only on highly active patches on the carbon surface. These are always saturated with adsorbed oxygen, and the rate of reaction

Time (hrs.).	Partial pressure of $O_2(P)$ 754 mm. Temperature (t) 40°.	$P = 176\cdot2$. $t = 40°$.	$P = 176\cdot2$. $t = 50°$.
1	2·3	2·0	3·5
1½	3·0	2·8	4·9
2	4·0	3·5	6·2
2½	4·3	4·2	7·6
3	5·4	4·9	9·0
3½	6·4	5·7	10·3
4	7·0	6·5	11·6
4½	7·8	7·3	12·9
5	8·4	8·0	14·3
5½	9·0	8·9	15·7
6	10·6	9·5	17·0
	$k = 0\cdot013$	$k = 0\cdot013$	$k = 0\cdot023$

measured is the rate of evaporation of carbon dioxide from them, a reaction of zero order (compare Langmuir, *J. Amer. Chem. Soc.*, 1916, **40**, 1361).

If we imagine the surface combustion as spreading out superficially as a ring, the rate of autoxidation should increase as the circumference of the ring increases; the reaction would thus be autocatalytic in behaviour. On the other hand, if it be imagined that combustion proceeds along a chain of carbon atoms, the zero order of such a combustion process is readily intelligible.

Substances strongly adsorbed by charcoal will be preferentially adsorbed on the most active areas of the charcoal surface, and since the rate of evaporation will be slow from such surfaces, it is possible to poison such areas preferentially. As poisons, potassium ferricyanide and amyl alcohol were employed. The adsorption isotherms were determined, the former colorimetrically and the latter by surface-tension measurements. The amounts of poison adsorbed by 100 mg. of charcoal necessary completely to arrest autoxidation are given in the following table :

Poison.	G.-mol. adsorbed by 100 mg. of charcoal.	No. of autoxidisable atoms per mg. of charcoal.
Potassium ferricyanide	$3\cdot6 \times 10^{-7}$	$3\cdot6 \times 10^{-9} \times 6\cdot06 \times 10^{23} = 2\cdot38 \times 10^{15}$
Amyl alcohol	$9\cdot0 \times 10^{-7}$	$9 \times 10^{-9} \times 6\cdot06 \times 10^{23} = 5\cdot45 \times 10^{15}$

The ferricyanide method probably gives the more accurate value, not only on account of the greater sensitivity of the colorimetric method for small concentrations, but also on account of the stronger adsorptive power of the charcoal for the ion rendering the action of poisoning more selective. Some uncertainty is introduced by the assumption that the ferricyanide ion occupies but one elementary atom on the carbon surface; since, however, the autoxidisable area is relatively small, the probability of two autoxidisable atoms being in contact with each other is remote.

The total area per mg. of charcoal was determined from the surface saturation value of amyl alcohol. For saturation, the fraction

of a gram-molecule of amyl alcohol adsorbed per mg. of charcoal was found to be 1.04×10^{-6}, hence the number of atoms on the surface of one mg. is 6.30×10^{17}; since the density of charcoal is 2.16, the surface per mg. of charcoal is 0.0266 square metre,* a value in good agreement with that given by Paneth and Radu (*Ber.*, 1924, 57, 1221), who obtained for similar charcoal an area of 0.0248 sq. metre per mg.

From the areas given by adsorption measurements the fraction of the surface autoxidisable is $2.38 \times 10^{15}/6.3 \times 10^{17} = 0.38\%$. The rate of autoxidation at $40°$ is 0.013 c.mm. of oxygen per mg. of charcoal per hour, equivalent to a carbon consumption of 3.51×10^{14} atoms per hour. Thus, the average life of one of the autoxidisable carbon atoms on the surface is $2.38 \times 10^{15}/3.51 \times 10^{14}$ or 7 hours. The mechanism of the autoxidation process may probably be represented most conveniently by the following equations :

$$C + 2H_2O + O_2 \longrightarrow C{<}^{OH—H \cdots O}_{OH—H \cdots O} \longrightarrow CO_2 + {}^{H_2O}_{H_2O}$$
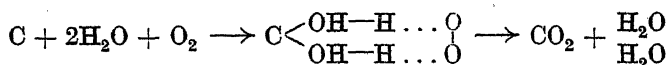
B. *The Catalytic Oxidation of Organic Acids.*

A consideration of the published data on the oxidation of oxalic acid and various α-amino-acids indicates that the conclusions already summarised (p. 1348) cannot be regarded as correct, although these relationships do obtain over a somewhat limited range of concentration.

The investigations of Langmuir make it probable that the oxygen molecule in the reactive state actually occupies two elementary spaces on the space lattice, thus justifying the square-root relationship obtained. There is little doubt that the substance undergoing oxidation is likewise adsorbed, but that the velocity of oxidation should be inversely proportional to its bulk concentration for extremely dilute solutions is improbable.

It is to be anticipated that, as in the combination of ethylene and hydrogen at nickel and copper surfaces (*J.*, 1922, **121**, 309) or the oxidation of sulphur dioxide at a platinum surface, the reaction velocity should be proportional to the surface concentrations of both reactants, and should thus attain to a maximum when the surface phase consists of an optimum mixture for reaction to occur, the velocity sinking on each side as one or other reactant is increased in quantity.

We have found that in aqueous solutions substances containing

* This calculation may also be performed in the following manner : Since the area of a benzene ring is 25Å (the maximum area parallel to the cleavage plane in graphite), the area for each atom is $25/6$Å, thus the area of 6.30×10^{17} atoms is 262 sq. cm. or 0.0262 sq. metre.

but one polar group, such as alcohol, formic, acetic, and the higher fatty acids, do not undergo oxidation at the surface of charcoal. On the other hand, substances containing two adjacent polar groups, one of which may be a mobile hydrogen atom, such as α-amino-acids, phenylthiocarbamide, oxalic and malonic acids, are readily oxidised, a similar phenomenon to that noted by Kruyt and van Duin (*Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 234) in their investigations on the acceleration of the removal of bromine from $\beta\beta$-dibromo-propionic acid in the presence of charcoal; whilst α-amino-acids undergo oxidation, monochloroacetic acid is not oxidised.

In confirmation of Warburg's work on the oxidation of oxalic acid the ratio of carbon dioxide evolved to oxygen adsorbed was found to be $4 : 1$, agreeing with the equation $2H_2C_2O_4 + O_2 = 4CO_2 + 2H_2O$. The temperature coefficient was $k_{50^\circ}/k_{40^\circ} = 2 \cdot 0$, compared with Warburg's value of $2 \cdot 1$ for iron-containing charcoal. Malonic acid also was oxidised, the ratio found, $CO_2/O_2 = 1 : 1$, agreeing with the equation

$$2CH_2(CO_2H)_2 + O_2 \longrightarrow 2CH(OH)(CO_2H)_2 \xrightarrow{O_2}$$
$$2CHO \cdot CO_2H + 2CO_2 + 2H_2O.$$
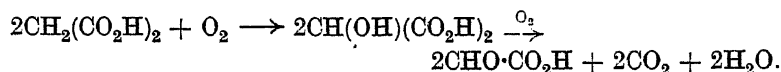
Glyoxylic acid was identified by the indole–sulphuric acid reaction. The reaction velocities of acid oxidation were much greater than the autoxidative process, although the temperature coefficients from which energies of activation are frequently calculated are likewise higher ($1 \cdot 8 : 2 \cdot 0$). This is an indication that the oxidation is proceeding on another portion of the charcoal, greater in extent than that undergoing autoxidation. This view was confirmed by showing that the two reactions, the autoxidation and the acid oxidation, were not coupled reactions * and that the autoxidisable areas could be poisoned selectively without interfering with the process of catalytic oxidation.

The influence of variation in the concentration of oxalic acid at constant oxygen pressures as well as the effect of an increase in oxygen pressure is shown in the curves in Figs. 1 and 2.

As was anticipated, the velocity rises to a well-defined maximum with increasing acid concentration, subsequently falling off as the

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* It is frequently assumed that *all* such reactions are coupled, involving the intermediate formation of hydrogen peroxide. On this hypothesis the above reaction could be written :

$$C + 2H_2O \rightarrow C\begin{array}{l}OH \cdot H\\OH \cdot H\end{array} \xrightarrow{O_2} C\begin{array}{l}OH \cdot H \cdot O \quad H \cdot O\\OH \cdot H \cdot O. \quad H \cdot O\end{array} + \begin{array}{l}COOH\\|\\COOH\end{array} \rightarrow 2CO_2 + 2H_2O.$$
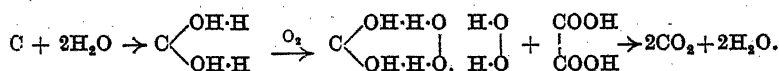
The addition of $M/1000$-potassium iodide, however, had no effect on the reaction velocity.

surface phase becomes deficient in oxygen or acid by displacement. The maximum velocity, which is attained when the surface is covered with acid and oxygen in suitable stoicheiometric proportions, is identical for the two gas pressures examined; this may be taken as proof that we are in reality dealing with a constant area of catalytic surface which is almost completely saturated with the two reactants, the displacement of the maximum towards higher oxalic acid concentrations at higher oxygen pressures representing the

FIG. 2.
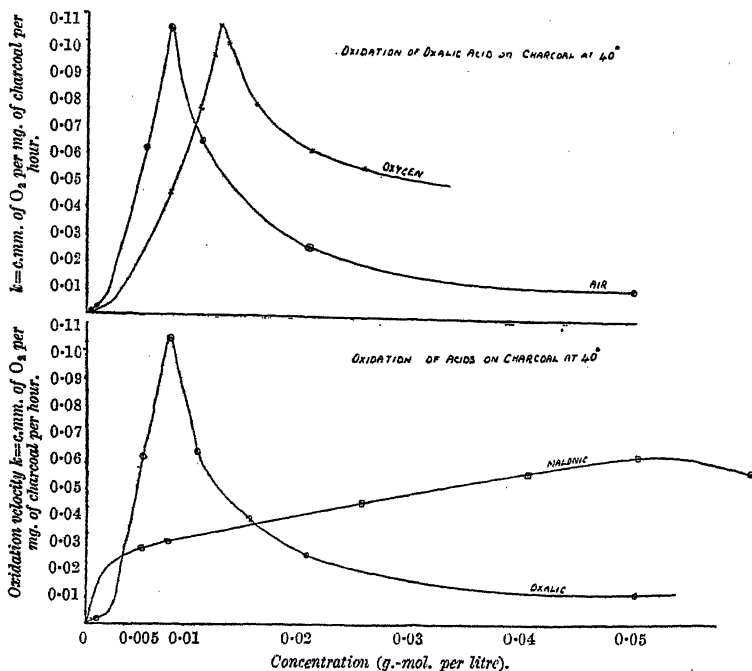
FIG. 1.

displacement of adsorbed oxalic acid by oxygen. The optimum concentration of acid under constant gas pressure does not appear to alter for an elevation of temperature of $10°$, an indication that the adsorptive unions between the reactants and charcoal are relatively strong and do not differ sensibly from one another. The adsorption isotherms for malonic and oxalic acids were determined for the charcoal, and the surface concentrations at the point of optimum velocity of oxidation were found to be as follows. The specific activities of the acids as measured by the value of $k_{max.}$ are inversely proportional to the amounts adsorbed.

Acid.	$k_{max.}$	C at $k_{max.}$ molarity.	Amount adsorbed (x), g.-mol. per mg. of charcoal.	$k_{max.} \times x.$
Oxalic	0·105	0·0075	$3·4 \times 10^{-7}$	$3·57 \times 10^{-8}$
Malonic	0·060	0·050	$5·9 \times 10^{-7}$	$3·54 \times 10^{-8}$

The extent of surface catalytically active was determined by the addition of amyl alcohol as poison until the reaction ceased, the adsorption of the amyl alcohol from the solution being determined by means of the surface tension (drop-weight method). When the catalytic activity ceased completely, owing to the selective adsorption of the alcohol, the amount adsorbed per mg. of charcoal was $4·2 \times 10^{-7}$ mol. Hence the number of catalytically active atoms per mg. is of the order $4·2 \times 10^{-7} \times 6·06 \times 10^{23} = 2·55 \times 10^{17}$ atoms, representing a fraction of the total area of $2·55 \times 10^{17}/ 6·30 \times 10^{17} = 40·5\%.$*

No very definite conclusions, however, can be drawn from the above data as to the surface concentrations of the two reactants on the active area, since the oxalic and malonic acids, when adsorbed on the active areas in suitable concentrations for optimum velocity of reaction, are doubtless adsorbed to some extent on the less active areas as well.

The determinations of the oxygen absorbed and of the carbon dioxide evolved, for very dilute solutions of oxalic acid, may be employed for calculating the effect of increasing oxalic acid concentration on the autoxidation as is indicated in Fig. 3. The autoxidation (curve 2) is gradually poisoned by the adsorbed oxalic acid; thus this substance poisons the autoxidisable areas in a manner analogous to that of other adsorbed solutes.

It is thus clear that very active areas may readily be distinguished from feebly active areas by selective poisoning, provided that the poison is adsorbed only by the active areas. For this purpose it is desirable to utilise small concentrations of strongly adsorbed poisons (although an upper limit to the strength of union poison–substrate is set by the necessity for obtaining true equilibrium in a relatively short space of time). Areas differing but little in activity can be distinguished from one another only by employing a number of poisons with different adsorption coefficients.

Interpretation of the Curves.

The definite maximum exhibited in the oxidation of oxalic acid at the surface of charcoal with increasing acid concentration indicates that both reactants must be adsorbed on a limited area of

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* This evidently represents a maximum for the catalytically active area, since poisoning is not necessarily quite selective in its action.

surface. If we denote the rate at which oxygen strikes the surface, which rate will be proportional to the oxygen pressure, by P_{O_2}, and the rate at which oxalic acid strikes the surface by C_{ox}, when equilibrium is established a fraction, θ_1, of the surface will be covered with oxygen and a fraction, θ_2, covered with oxalic acid, the remainder, θ, being covered with water which the reactants can displace. If v_1 and v_2 be the specific rates of desorption of the reactants and α_1 and α_2 the coefficients of reflection, then, on the

FIG. 3.

OXIDATION OF OXALIC ACID IN DILUTE SOLUTIONS IN AIR AT 40°
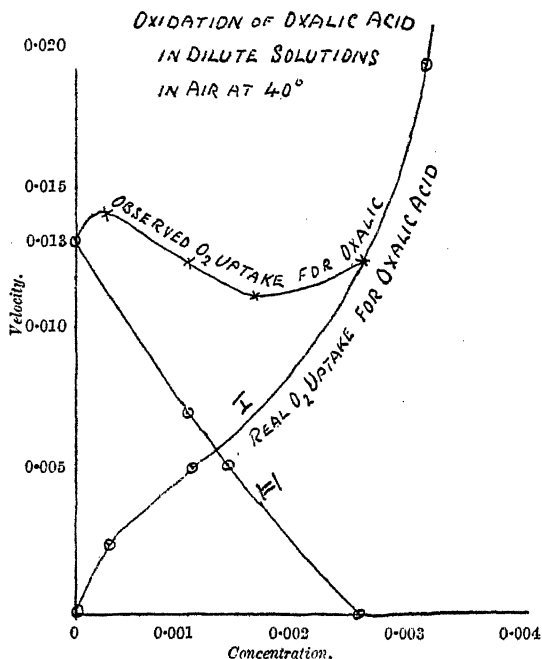
assumption that the oxygen molecule occupies two elementary spaces on the lattice and the oxalic acid but one, at equilibrium we obtain

$$(1) \quad \alpha_1 P_{O_2}\theta^2 = v_1\theta_1{}^2 \text{ and } \alpha_2 C_{ox}\theta = v_2\theta_2 \quad . \quad . \quad . \quad (2)$$

The rate of chemical action between oxalic acid and oxygen on the surface will be

$$dx/dt = k\theta_1\theta_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Also

$$\theta + \theta_1 + \theta_2 = 1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Hence, eliminating θ_1, θ_2, and θ,

$$\frac{dx}{dt} = k\left(\sqrt{\frac{\alpha_1 P_{O_2}}{v_1}}\right)\left(\frac{\alpha_2}{v_2} \cdot C_{ox}\right)\theta^2 = \frac{k'\sqrt{P_{O_2}}C_{ox}}{(1 + m\sqrt{P_{ox}} + nC_{ox})^2}$$

For small concentrations of oxygen and oxalic acid this equation reduces to $dc/dt = k\sqrt{P_{O_2}}C_{OX}$. As the oxygen pressure increases and the oxalic acid concentration remains small, we obtain $dc/dt = kC_{OX}/\sqrt{P_{O_2}}$. This portion of the curve is experimentally realised at the commencement.

At the other end of the curve, where the surface is approaching saturation in oxalic acid and the oxygen pressure is relatively low, the expression reduces to $dx/dt = k\sqrt{P_{O_2}}/C_{OX}$, the form obtained by Warburg and his co-workers; this is exemplified in the curves in the region for high oxalic acid concentrations; whilst when the oxygen pressure and oxalic acid concentration are commensurate with each other and are both large the curve evidently passes through a maximum value independent of P_{O_2} or C_{OX}, a phenomenon likewise apparent from the experimental data.

UNIVERSITY OF CAMBRIDGE.

CLXXXV.—*The Isomerism of the Oximes. Part XXII. The Configuration of the Aldoximes.*

By OSCAR L. BRADY and GERALD BISHOP.

THE configuration of the aldoximes, as generally accepted, is based on a method of determination first suggested by Hantzsch (*Ber.*, 1891, **24**, 13), though the procedure has been subsequently somewhat modified. It depends upon the fact that acetic anhydride at a temperature not above 30° converts both isomerides into acetyl derivatives, and that on subsequent treatment of these compounds with dilute sodium hydroxide one is converted into the nitrile, whilst the other is hydrolysed with the reformation of the original oxime; the term *syn* was assigned to the former class, since it was held that the elimination of acetic acid would take place more readily if the H and OAc were contiguous, whilst the term *anti* was given to the latter compounds.

$$R{\cdot}CH \xrightarrow[\text{NaOH}]{Ac_2O} \quad R{\cdot}CH \qquad R{\cdot}CH \qquad R{\cdot}CH \quad \longrightarrow \quad RCN$$
$$HO{\cdot}N \xleftarrow{} AcO{\cdot}N \qquad N{\cdot}OH \xrightarrow{Ac_2O} N{\cdot}OAc \qquad +HOAc$$
$$\textit{anti}\text{Aldoxime.} \qquad\qquad \textit{syn}\text{Aldoxime.}$$
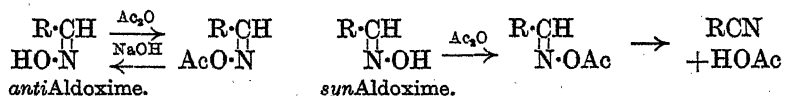
The assumption which Hantzsch made has the virtue of simplicity, but the subsequent discovery of *trans*-addition and -elimination in ethylenic compounds has demonstrated the danger of assuming *cis*-elimination merely on account of its simplicity. Recently the case for *trans*-elimination has been put by several workers, particularly by Beckmann, Liesche, and Correns (*Ber.*,

1923, **56**, 341) on theoretical grounds and by von Auwers and Ottens (*Ber.*, 1924, **57**, 446) from a study of the optical properties of the aldoximes and their ethers. For similar reasons, doubt has been thrown by Meisenheimer and his co-workers (*Ber.*, 1921, **54**, 3195, 3206; 1924, **57**, 276, 282, 289) on the view that in the Beckmann change of ketoximes the vicinal groups are interchanged. They found that 3 : 4 : 5-triphenyl*iso*oxazole (I), on treatment with ozone followed by water, gave benzoyl-β-benzilmonoxime (II), which could be hydrolysed to β-benzilmonoxime and could be regenerated by benzoylation of the β-oxime. Now the configuration (II) is that usually assigned, on the basis of the Beckmann change, to benzoyl-α-benzilmonoxime, and it is accordingly suggested that the configuration of these compounds should be reversed and that the Beckmann change takes place in a *trans* and not a *cis* sense.

$$\text{(I.)} \quad \begin{array}{c} C_6H_5 \cdot C \text{———} C \cdot C_6H_5 \\ N \cdot O \cdot C \cdot C_6H_5 \end{array} \rightarrow \begin{array}{c} C_6H_5 \cdot C \text{———} CO \cdot C_6H_5 \\ N \cdot O \cdot CO \cdot C_6H_5 \end{array} \text{(II.)}$$

This argument is, however, open to criticism in view of the peculiar behaviour of oximes on benzoylation. The stable cinnam*syn*- and *o*-methoxycinnam*syn*-aldoximes are converted into the benzoyl derivatives of the corresponding *anti*aldoximes on benzoylation (Brady and Thomas, J., 1922, **121**, 2104; Brady and Grayson, J., 1924, **125**, 1419) and in a subsequent paper it will be shown that this reaction is a general one. Although the doubt has been partly removed by Meisenheimer, some still exists regarding the constitution of the compound obtained by the benzoylation of α-benzilmonoxime owing to the fact that the oxime cannot be · regenerated therefrom by hydrolysis. Consequently, although the above work seems conclusive, it cannot be accepted without reservation. A second instance is adduced by Meisenheimer in support of his views. *o*-Aminobenzophenoneoxime exists in two forms, only one (III) of which gives the benzo*iso*-oxazole (IV) on diazotisation. Here again the results are contrary to those indicated by a *cis*-Beckmann change, since (III) gives the anilide of anthranilic acid. The following mechanism. was suggested :

$$\begin{array}{ccc} \begin{array}{c} -CPh \\ NH_2 \ HO \cdot N \end{array} & \xrightarrow{HNO_2} & \begin{array}{c} -CPh \\ \diagdown / -N(:N) \cdot O \cdot N \end{array} & \begin{array}{c} \diagup -CPh \\ \diagdown / -O-N \end{array} \\ \text{(III.)} & & & \text{(IV.)} \end{array}$$

but the reaction might be interpreted in another way using the alternative configuration :

Meisenheimer tried to use benzo*isoo*xazole formation from the oximes of ortho-halogen substituted benzophenones to determine their configuration, but was unable to obtain two isomerides of *o*-chloro- or *o*-bromobenzophenoneoxime (compare also von Auwers and Jordan, *Ber.*, 1925, **58**, 26).

No fresh evidence of a purely chemical nature has, however, been forthcoming concerning the configuration of the aldoximes and it seemed likely that the action of alkalis on ortho-halogen substituted aldoximes might afford information. In this case the benzo*isoo*xazole cannot be isolated, undergoing tautomeric change to the hydroxynitrile. For example, this compound was obtained in attempts to prepare the benzo*isoo*xazole by the following reaction :
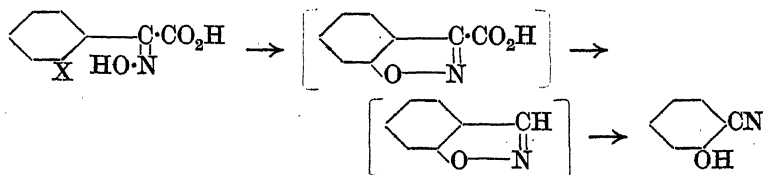
where $X = Br$ or NO_2 (Russanow, *Ber.*, 1892, **25**, 3297; V. Meyer, *Ber.*, 1893, **26**, 1256). Similarly, Bone (J., 1893, **63**, 1346) obtained 5-nitrosalicylonitrile by heating 5-nitro-*o*-chlorobenz*anti*aldoxime with 22% sodium carbonate for 2—3 hours at 120°.
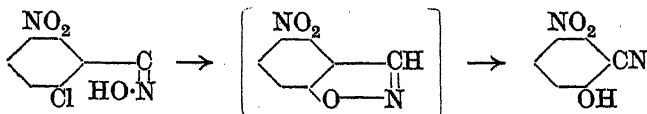
(Compare also the similar behaviour of the *isoo*xazoles, Claisen and Stock, *Ber.*, 1891, **24**, 130; Claisen, *Ber.*, 1903, **36**, 3664.)

Neither of the isomeric *o*-chlorobenzaldoximes reacts sufficiently readily to be satisfactory for the purpose, but the introduction of a nitro-group renders the chlorine more reactive, and the study of the isomeric 2-chloro-5-nitrobenzaldoximes has lead to interesting results. The *anti*-isomeride (according to Hantzsch) does not give any ionisable chlorine when heated at 50° for 4 hours with $0\cdot25N$-sodium hydroxide, whilst under the same conditions the *syn*-isomeride yields 27% of its chlorine in an ionised form after 1 hour, 45% after 2 hours, and 53% after 4 hours. Boiling with

N-sodium hydroxide for 30 minutes brought about slight change in the *anti*-isomeride, whilst the *syn*-compound was completely converted into 5-nitrosalicylonitrile. There is no doubt, therefore, that the so-called *syn*-isomeride is more readily converted through the unstable benzo*iso*ooxazole into the hydroxy-nitrile than the *anti*-isomeride. Since it is reasonable to suppose that ring formation will occur more readily when the hydroxyl group is vicinal to the halogenated benzene ring, this result involves the reversal of the configuration of the aldoximes in accordance with the views of Meisenheimer, Beckmann, and von Auwers.

Two alternatives, however, need consideration. The sodium salt of the so-called *syn*-oxime may be represented as (V), the elimination of sodium chloride then giving (VI);
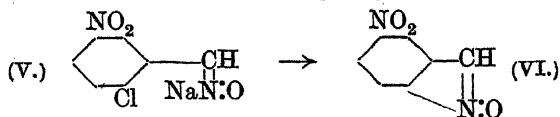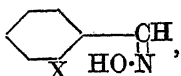
but it does not seem likely that this compound would give the hydroxy-nitrile so readily. The second is that the halogen is first removed by hydrolysis, giving (VII); then follow a kind of salt formation (VIII) and subsequent loss of water to give the benzo-*iso*ooxazole and hence the hydroxy-nitrile as suggested above for the aminobenzophenoneoxime.
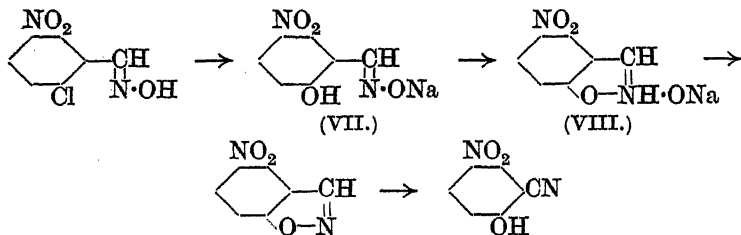
This seems unlikely, since the halogen is not readily removed by hydrolysis from the *anti*-oxime nor from 2-chloro-5-nitrobenzo-nitrile nor from 2-chloro-5-nitrobenzoic acid.

Any isomeric change, apart from tautomerism, in the oximes would take place in the direction *syn* to *anti* or reactive to un-reactive form, for in our work on the aldoximes no indication of a change in the reverse direction under these conditions has been observed in the many cases of substituted benzaldoximes investigated. This change probably accounts for the slowing of the reaction and its apparent departure from the law of mass action. The only point in doubt in this connexion is that during the change *syn* to *anti* the molecule may be in a particularly reactive state.

As a result of this work it appears doubtful whether Hantzsch's assumption that *cis*-elimination of acetic acid takes place from the acetyl derivatives of the aldoximes can be maintained, and, taken in conjunction with the investigations of Meisenheimer, there are considerable grounds for suggesting that the configurations of all these compounds should be reversed. There is also some collateral evidence in support of such reversal (which will be discussed in subsequent communications), notably perhaps the difficulty often experienced in obtaining the so-called *syn*-isomerides of ortho-substituted benzaldoximes ; if these have the structure , their non-formation may be due to steric hindrance. Such a reversal, at the present time, would lead to great confusion, and further work is being undertaken which may lead to a reconsideration. For this reason, we propose to adopt in future the following convention. The aldoximes will be designated α- and β-, the α-oxime being that which on treatment with acetic anhydride at 30° gives an acetyl derivative which on hydrolysis regenerates the original oxime, whilst the β-oxime is that which under the same conditions gives the nitrile or the corresponding acid ; α-acyl derivatives are those which on hydrolysis regenerate the oximes, β-acyl derivatives those which give the nitrile or acid ; α-*O*-ethers are those prepared from α-oximes, β-*O*-ethers those prepared from β-oximes, there being at present no method by which the configuration of these compounds can be directly ascertained.

EXPERIMENTAL.

α-2-*Chloro*-5-*nitrobenzaldoxime*.—A mixture of 2-chloro-5-nitrobenzaldehyde (5 g. ; prepared by the nitration of *o*-chlorobenzaldehyde; Erdmann, *Annalen*, 1893, **272**, 153), sodium acetate (5 g.), and hydroxylamine hydrochloride (2 g.) in alcohol (100 c.c.) was heated for 2 hours under reflux. The oxime was precipitated with water and crystallised from benzene. Its configuration was determined by the Hantzsch method—dissolution in acetic anhydride at room temperature and shaking with sodium carbonate ; the solid separating was crystallised from dilute alcohol, when α-*acetyl-2-chloro-5-nitrobenzaldoxime* was obtained as a pale buff, microcrystalline powder, m. p. 110° (Found : N, 11·7. $C_9H_7O_4N_2Cl$ requires N, 11·5%). When this compound was warmed with 2*N*-sodium hydroxide until it dissolved, and the solution saturated with carbon dioxide, the original oxime was obtained.

β-2-*Chloro*-5-*nitrobenzaldoxime*.—When hydrogen chloride was passed into a chloroform or ethereal solution of the α-oxime, no

hydrochloride was formed (compare 2 : 4-dinitrobenzaldoxime : Wentworth and Brady, J., 1920, **117**, 1040; Brady and Manjunath, J., 1924, **125**, 1066). Transformation was, however, brought about by Dunstan and Thole's method, but it was essential to use sufficient hydrochloric acid to ensure complete solution. The α-oxime (4 g.) was ground with concentrated hydrochloric acid (100 c.c.), the mixture cooled in ice and saturated with hydrogen chloride. The clear solution was poured into a large excess of 2N-sodium carbonate. The dried precipitate, after crystallising three times from benzene, gave β-2-*chloro-5-nitrobenzaldoxime* in very pale yellow needles, m. p. 176° (Found : N, 14·1. $C_7H_5O_3N_2Cl$ requires N, 14·0%). This was oriented in a similar way to the α-oxime; the acetyl derivative was not, however, isolated pure, but was hydrolysed at once, when ammonia and 2-chloro-5-nitrobenzoic acid were obtained.

Action of Alkali on α- *and* β-2-*Chloro-5-nitrobenzaldoximes.*—A solution of the α-oxime (0·25 g.) in N-sodium hydroxide (10 c.c.) was boiled under reflux for 30 minutes, cooled, and saturated with carbon dioxide, when 0·15 g. of the original oxime was recovered. The filtrate on acidification gave a small amount of 5-nitrosalicyclic acid. The β-oxime, treated similarly, gave with carbon dioxide a precipitate which, after crystallisation from water, was identified as 5-nitrosalicylonitrile, whilst the solution on acidification gave a small amount of 5-nitrosalicylic acid. With 0·5N-sodium hydroxide at 50°, the α-oxime gave no chlorine ions after 4 hours. In the case of the β-oxime 0·632 g. was dissolved in 100 c.c. of 0·25N-sodium hydroxide at 50° and kept at that temperature in a thermostat; 25 c.c. were removed from time to time, acidified with dilute nitric acid, and the ionised halogen at once determined by Volhard's method. After 1 hour 27% of the halogen was in the ionised form, after 2 hours 45%, and after 4 hours 53%.

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CLXXXVI.—*A Spectroscopic Study of the Combustion of Phosphorus Trioxide and of Hydrogen Phosphide.*

By HARRY JULIUS EMELÉUS.

THE spectroscopic investigation of the light emitted in many chemical reactions is a direct way of examining the mechanism of chemical change, although an extensive application of this method is hindered by the complex nature of most processes of

combustion and by our still scanty knowledge of the origin of spectra. Flames may be arbitrarily divided into two groups. The first comprises ordinary hot flames, in which light emission may be influenced by little-known temperature factors. The second is the class of phenomena termed chemiluminescence, which includes chemical reactions emitting light without any considerable rise in temperature (e.g., below 200°). In this case it is more certain that the radiation has its origin in the chemical process, and the interpretation of the spectra observed is consequently more readily carried out.

The oldest recorded example of chemiluminescence is the slow oxidation of phosphorus at room temperature. The light emitted was found by Centnerszwer and Petrikaln (Z. physikal. Chem., 1912, **80**, 235) to give a continuous spectrum in the visible region,

Fig. 1.

Fig. 2.

Fig. 3.
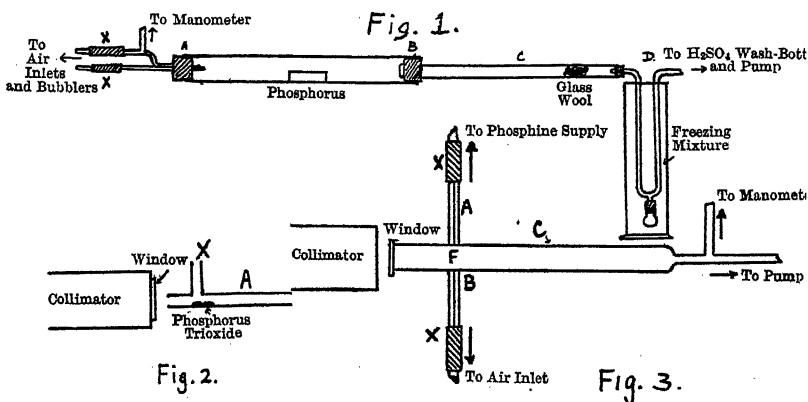
and to show five bands (or groups of lines) in the ultra-violet at about $\lambda = 3270, 2600, 2530, 2470, 2390$ Å.U. This light gives essentially the same band spectrum as that obtained from phosphorus burning normally, or under reduced pressure with a flame temperature of 125° (Emeléus and Downey, J., 1924, **125**, 2491). In the experiments described below, the light from phosphorus trioxide slowly oxidising at the ordinary temperature and the flame of pure hydrogen phosphide burning under various conditions have been investigated, since they exhibit certain chemical anomalies in common with the slow oxidation of phosphorus, which are more fully discussed subsequently.

Preparation of Material.—The method of preparation of phosphorus trioxide described by Thorpe and Tutton (J., 1890, **57**, 545) was modified as follows :

Phosphorus was burnt *under reduced pressure* in the hard glass tube A B (2·5 cm. × 40 cm.) (Fig. 1). The air inlets were controlled

by screw clips at X X, and bubblers containing water were attached. A mercury manometer, connected as shown, was used to record the pressure. The tube C for condensing phosphorus pentoxide, and the U-tube D for collecting the product were as described by Thorpe and Tutton, but C was maintained at 50° by several Bunsen burners instead of by the use of a special hot water-jacket. Such a quantity of phosphorus (about 50 g.) was used that the molten material did not approach within 5 cm. of A. The best yields resulted when the flame was burning as a vertical yellow disk at a pressure of 30—40 cm. of mercury.

About 4 g. of phosphorus trioxide were produced consistently from 40—50 g. of phosphorus in 2—3 hours by this method, the apparatus requiring little attention. The product was volatilised from reduced copper gauze at 100—140° in a stream of dry carbon dioxide. The material so obtained melted at 22·0—22·5° to a colourless liquid, free from suspended matter.

The relatively large yield of phosphorus trioxide obtained by this method is possibly due to the rapid removal of the trioxide from the hot zone (it decomposes at 200°), coupled with a decrease in the flame temperature owing to the limited air supply.

Pure hydrogen phosphide was prepared by dropping water on phosphonium iodide.

The Spectrum of the Light from Glowing Phosphorus Trioxide.

Preliminary work showed that (i) the glow of phosphorus trioxide does not normally occur at its surface, as in the case of phosphorus, but appears as luminous pulses, often starting at considerable distances from the oxide, (ii) water vapour is essential to the glow, and the pulses occur more readily in presence of a little liquid water.

The apparatus finally adopted is illustrated in Fig. 2. The glass tube A, of 3 mm. internal diameter, was supported in correct alignment with the collimator slit, which was protected by a quartz window 2 mm. thick. The tube was first moistened, and one or two drops of molten phosphorus trioxide were introduced at X. It was warmed electrically to 30—40° by a resistance mat placed underneath, and a series of bright pulses was maintained by a slight draught. The tube was washed and recharged as each successive quantity of oxide became exhausted (generally after about 40 minutes). An exposure of 280 hours was recorded on a rapid plate, a copper arc spectrum being used for reference purposes, and the plate was sensitised before development by Wood's method (Astrophys. J., 1908, 27, 379).

The spectrum is identical with that obtained in the case of glowing phosphorus (Eme1éus and Downey, loc. cit.). The five

ultra-violet bands are fainter, but their relative intensities agree with those in the glow spectrum of phosphorus, as far as can be judged without elaborate photometric measurements.

The Spectrum of pure Hydrogen Phosphide burning spontaneously under Reduced Pressure in Air.

The apparatus shown in Fig. 3 was used. The tube C, of about 1 cm. internal diameter, had two capillary tubes, A, B, serving as inlets for the phosphide and air, sealed at about 5 cm. from the ground end, to which a quartz window, 2 mm. thick, was attached with wax. Connexion was also made to a water-pump and mercury manometer as shown. Ignition of the phosphide occurred spontaneously as the two gas streams entered the region of reduced pressure. The rate of supply of the gases was controlled by screw clips on the rubber connexions at X, X, and was so adjusted that a steady greenish-white flame resulted at F, the pressure being 3—8 cm. of mercury. Owing to the formation of a red decomposition product, the apparatus was cleaned and replaced every hour. An exposure of 20 hours was made, the further treatment of the plate being as described before. The temperature of the flame, measured by a thermometer inserted in place of the quartz window, varied between 160° and 230°. Luminosity will occur even at 40—60° if the velocities of the two gas streams are small, but it is very feeble.

The spectrum shows all the ultra-violet bands of the spectrum of glowing phosphorus and of phosphorus trioxide, and no others. It closely resembles that of phosphorus burning under reduced pressure in air (Emeléus and Downey, *loc. cit.*). In the spectra of the low-temperature flames the band at about $\lambda = 3270$ Å.U. is relatively more intense than in the glow spectra. This point will be referred to later.

If the vapour of acetone or ether is allowed to mix with the ingoing air when the phosphide flame is burning steadily at about 50°, it first produces an intermittent luminescence, the pulses then become less frequent and finally cease. When the supply of inhibiting vapour is stopped, the same phenomena are observed in the reverse order. Ether and acetone are particularly active poisons : the latter dimmed a flame even at 180°. Benzene, chloroform, coal gas, and ammonia act less effectively. A closer examination of this interesting phenomenon is being made.

The Spectrum of Hydrogen Phosphide burning at a Jet in Oxygen at Atmospheric Pressure.

With an exposure of 5 minutes the band at $\lambda = 3270$ Å.U. is observed, in addition to a strong and apparently continuous back-

ground. With a 15-minute exposure the four bands at $\lambda = 2600$, 2530, 2470, 2390 Å.U. are visible, and also two bands at about $\lambda = 3060$, 2800 Å.U. The latter are generally ascribed to water, and their presence is to be expected from the nature of the reaction. They are not excited in the low-temperature combustion of hydrogen phosphide, which is in agreement with van de Stadt's observation that free hydrogen is formed (compare van 't Hoff, " Studies in Chemical Dynamics," 1896).

Discussion of Results.

A very close analogy exists between the phenomena of the slow luminous oxidations of phosphorus and of phosphorus trioxide· Both can occur at room temperature, and are accompanied by the production of ions and ozone (compare Downey, J., 1924, **125**, 347). Rinde (*Arkiv Kemi, Min., Geol.*, 1918, **7**, No. 7) found that the ions produced in the latter case have approximately the same mobilities and coefficient of recombination as the ions from oxidising phosphorus (Bloch, *Ann. Chim. Phys.*, 1905, **4**, 25). Scharff (*Z. physikal. Chem.*, 1908, **62**, 179) pointed out that those substances which inhibit the oxidation and luminosity of phosphorus act in precisely the same way in the case of phosphorus trioxide. His contention that a boundary pressure exists, similar to that which is well known in the case of phosphorus, above which luminosity will not occur in pure oxygen, is not confirmed by Rinde (*loc. cit.*). In the author's experience these experiments give such inconsistent results that a final conclusion is not yet justifiable.

The glow of phosphorus and that of phosphorus trioxide differ sharply with regard to the necessity for the presence of water. Phosphorus glows readily in air or rarefied oxygen dried by passage over phosphorus pentoxide, but no luminosity occurs up to 60° for phosphorus trioxide under these conditions. Moreover, drying by strong sulphuric acid causes a big decrease in the brightness of the glow in the latter case. A slow non-luminous oxidation of phosphorus trioxide to phosphorus pentoxide has, however, been shown to occur when absence of water vapour prevents luminosity (Rinde, *loc. cit.*).

The suggestion that water plays an essential part in the luminous oxidation of phosphorus trioxide was made by Schenck, Mihr, and Banthien (*Ber.*, 1906, **39**, 1506). Rinde put forward the hypothesis that hydrogen phosphide is first formed by interaction of phosphorus trioxide and water, and is then oxidised with luminescence. Since phosphorus trioxide is known to be formed in the slow oxidation of phosphorus, the same view could be applied to the case of glowing phosphorus, provided water were present. It is

known, moreover, that spontaneously inflammable hydrogen phosphide results from the interaction of phosphorus trioxide and water at 90°, and this reaction might be supposed to occur to the necessary limited extent at room temperature. Indirect evidence that such is the case is afforded by the behaviour of hydrogen phosphide outlined below, but a direct demonstration of the reaction is still lacking.

Hydrogen phosphide and oxygen react only very slowly at ordinary pressures, but when the pressure is reduced an explosion occurs (compare van 't Hoff, op. cit.). Also, experiments described above show that certain substances can inhibit the ignition of the phosphide when the pressure of phosphide–air mixtures is reduced, these substances being all inhibitors of the glows of phosphorus and of its trioxide. In addition, the pulsating effect produced by inhibiting substances on the flame of hydrogen phosphide seems closely parallel to Lord Rayleigh's observations with phosphorus (Proc. Roy. Soc., 1921, A, 99, 372, et seq.).

The foregoing review of the anomalies which are in some measure common to the low-temperature oxidation of phosphorus and of its two compounds appears to be in complete agreement with the spectroscopic results. That these three oxidation processes should give the same light emission, coupled with the fact that they have so much else in common, renders it very probable that there is something produced in each case responsible for the chemical peculiarities, and intimately connected with the luminosity. The spectroscopic evidence does not justify the assumption that the chemical processes themselves are identical : further chemical evidence is needed to decide that. It does, however, show that some excited system is produced in each of the chemical reactions studied, which radiates the ultra-violet band spectrum observed.

There are a few relevant points with regard to the light itself. The apparently continuous visible radiation in each case has yet to be accounted for. From the fact that a band spectrum is produced, and not a line spectrum, it may be concluded that this is of molecular origin. The band at about $\lambda = 3270$ Å.U. was observed by Hartley (Phil. Trans., 1894, 185, 168) on volatilising phosphorus pentoxide in the oxy-hydrogen flame, and Petrikaln (Z. Physik, 1924, 22, 119) has drawn attention to the presence of the five bands in the spectrum produced by phosphorus pentoxide in the carbon arc. These observations render it probable that the molecule responsible is that of phosphorus or of a phosphorus oxide. If it were possible to analyse the bands and so find the moment of inertia of the radiating system, its nature might be settled, but there appears to be no immediate prospect of this.

As stated above, the band at about $\lambda = 3270$ Å.U., compared

with the remaining four bands, is relatively less intense in the glow spectra of phosphorus and of its trioxide than in that of phosphorus or hydrogen phosphide burning under reduced pressure. The reason for this striking result can only be surmised : it may be that this band is due to a different chemical compound from the others, but it could equally well arise from the influence of physical conditions on the occurrence of the various quantum transitions.

Summary.

1. A modification of Thorpe and Tutton's method of preparing phosphorus trioxide is described.

2. A spectroscopic study of the light from glowing phosphorus trioxide, from pure hydrogen phosphide burning spontaneously in air under reduced pressure, and from the pure phosphide burning in oxygen, has been made. In each case the ultra-violet band spectrum is identical with that of glowing phosphorus, and of the element burning normally. A variation in the relative intensity of the bands with the conditions has been noted.

3. Certain substances which inhibit the glow of phosphorus and of phosphorus trioxide can prevent the ignition of a hydrogen phosphide–air mixture when the pressure is reduced.

4. It is suggested that the low-temperature combustions of phosphorus, phosphorus trioxide, and hydrogen phosphide involve some common stage responsible for the chemical anomalies and intimately bound up with the characteristic light emission.

CLXXXVII.—*The Action of Phosphorus Pentachloride on* 2-iso*Nitroso-1-hydrindones.*

By ROBERT DOWNS HAWORTH and HERBERT SHEPPARD PINK.

IN the preparation of 4 : 5-dimethoxyhomophthalic acid from an ethereal suspension of 2-*iso*nitroso-5 : 6-dimethoxy-1-hydrindone and phosphorus pentachloride, at the stage at which the product

was poured into ice-water, the ethereal solution contained a sub-. stance which gave the required acid on hydrolysis but was not further investigated (Perkin and Robinson, J., 1907, **91**, 1082); the authors suggested, however, that it might be 4 : 5-dimethoxy-homophthalimide (I), produced by a Beckmann rearrangement of the *iso*nitroso-compound.

We have now isolated the intermediate product and found that, although its composition is that of dimethoxyhomophthalimide, its properties differ in some respects from those characteristic of homo-phthalimide derivatives; for example, the substance is readily soluble in organic solvents and in sodium bicarbonate, and is rapidly hydrolysed on warming with sodium hydroxide or dilute sulphuric acid. It therefore seemed probable that the substance is 2-*carboxy*-4 : 5-*dimethoxyphenylacetonitrile* (II). This view was confirmed by the observation that alkaline hydrogen peroxide con-verts it into 4 : 5-*dimethoxyhomophthalamic acid* (III), which is then converted into 4 : 5-dimethoxyhomophthalimide (I) on heating. This is an insoluble, high-melting substance identical with the product of the action of heat on ammonium 4 : 5-dimethoxy-homophthalate.

Similarly, the intermediate compound produced by the action of phosphorus pentachloride on 2-*iso*nitroso-1-hydrindone is *o*-carboxyphenylacetonitrile, identical with the acid obtained by the action of potassium cyanide on phthalide (Wislicenus, *Annalen*, 1886, **233**, 102). It is converted by the action of alkaline hydrogen peroxide into homophthalamic acid, and this yields homophthalimide on being heated at 200°.

2-*Carboxy*-4 : 5-*methylenedioxyphenylacetonitrile* (as II) has been obtained from 2-*iso*nitroso-5 : 6-methylenedioxy-1-hydrindone, and from it the corresponding *homophthalamic acid* (as III) and *homo-phthalimide* (as I) have been prepared.

The yields of the *o*-carboxyphenylacetonitriles obtained under the conditions outlined are good and this method appears to be the most convenient for the preparation of these substances.
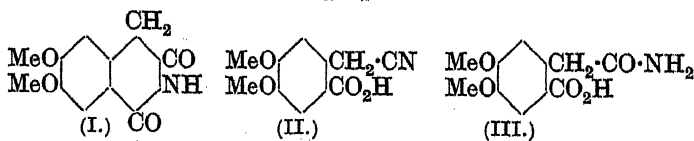
E X P E R I M E N T A L.

o-Carboxyphenylacetonitrile.—2-*iso*Nitroso-1-hydrindone and phos-phorus pentachloride were allowed to react under the conditions described by Perkin and Robinson (*loc. cit.*). The reaction mixture

was poured on to ice, and the o-carboxyphenylacetonitrile collected; a further quantity was extracted from the filtrate with ether. It crystallised from hot water in colourless needles, m. p. 126° (decomp.) and did not depress the m. p. (124°; decomp.) of a sample prepared by Wislicenus's method (*loc. cit.*) and thrice crystallised from water.

Homophthalamic acid was prepared by treating a solution of o-carboxyphenylacetonitrile (7 g.) in a very slight excess of N-sodium hydroxide with a 3% solution of hydrogen peroxide at room temperature for 6 hours and acidifying the product with concentrated hydrochloric acid. The precipitated homophthalamic acid (7 g.), after being washed with water, crystallised from alcohol in colourless needles, m. p. 186°.

Homophthalimide was prepared in quantitative yield by heating homophthalamic acid at 200° until the evolution of water was complete. The residue crystallised from glacial acetic acid in pale yellow needles, m. p. 233°.

2-*Carboxy*-4 : 5-*dimethoxyphenylacetonitrile* (II) was prepared from dimethoxy*iso*nitrosohydrindone in the same way as its analogue. After two crystallisations from aqueous alcohol, the acid was obtained in long, colourless needles, m. p. 164—165° (decomp.) (Found : C, 59·8; H, 5·0. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). It is sparingly soluble in ether or hot water, but readily soluble in alcohol or acetic acid. When boiled with sodium hydroxide solution or with dilute sulphuric acid, it gives 4 : 5-dimethoxyhomophthalic acid, which crystallises from alcohol in needles, m. p. 223—224° (Perkin and Robinson, *loc. cit.*, give 215°); low figures are always obtained unless the intermediate carboxyphenylacetonitrile is purified. However, the homopiperonylimide, m. p. 178°, of the acid melting at 215° is identical with that prepared from the pure acid, m. p. 224°.

4 : 5-*Dimethoxyhomophthalamic acid* (III), prepared in the same way as its analogue, is insoluble in water, and crystallises from alcohol in colourless prisms, m. p. 204° (decomp.) (Found : C, 55·3; H, 5·5. $C_{11}H_{13}O_5N$ requires C, 55·2; H, 5·4%).

4 : 5-*Dimethoxyhomophthalimide* (I) was prepared by heating the homophthalamic acid at its m. p. for a few minutes, and also by heating ammonium 4 : 5-dimethoxyhomophthalate at 210°. It is sparingly soluble in organic solvents, but separates from glacial acetic acid in pale yellow needles, m. p. 245° (Found : C, 59·6; H, 5·0. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%).

2-*Carboxy*-4 : 5-*methylenedioxyphenylacetonitrile*, prepared in the same way as its analogues, is sparingly soluble in water, ether, benzene, or alcohol, but crystallises from much alcohol in minute prisms, m. p. 195—196° (decomp.) (Found : C, 58·6; H, 3·5.

$C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%). It is hydrolysed to 4 : 5-methylenedioxyhomophthalic acid, m. p. 236°, on warming with dilute acids or alkalis.

4 : 5-*Methylenedioxyhomophthalamic acid*, obtained in the same way as homophthalamic acid, crystallises from much alcohol in small rectangular prisms which soften at 230°, darken at 280°, and melt at 295°, which is the melting point of the corresponding homophthalimide (Found : C, 53·9; H, 4·1. $C_{10}H_9O_5N$ requires C, 53·8; H, 4·0%).

4 : 5-*Methylenedioxyhomophthalimide*, obtained by heating the homophthalamic acid at 200° for 15 minutes, crystallises from glacial acetic acid in yellow prisms, m. p. 295° (darkening at 280°) (Found : C, 58·6; H, 3·6. $C_{10}H_7O_4N$ requires C, 58·5; H, 3·4%).

CLXXXVIII.—*Studies of Dynamic Isomerism. Part XVIII. The Mechanism of Mutarotation.*[*]

By THOMAS MARTIN LOWRY.

1. *Mutarotation due to Isomeric Change.*

(a) The explanation that is now generally accepted of the mutarotation of the sugars is illustrated in the following scheme I.

(I.)

$$
\begin{array}{ccccc}
\text{CH}_2\text{·OH} & & \text{CH}_2\text{·OH} & & \text{CH}_2\text{·OH} \\
\text{CH·OH} & & \text{CH·OH} & & \text{CH·OH} \\
\text{CH} & & \text{CH·OH} & & \text{CH} \\
\text{CH·OH} & \rightleftharpoons & \text{CH·OH} & \rightleftharpoons & \text{CH·OH} \\
\text{CH·OH} & & \text{CH·OH} & & \text{CH·OH} \\
\text{C} & & \text{CHO or CH(OH)}_2 & & \text{C} \\
\end{array}
$$

_____
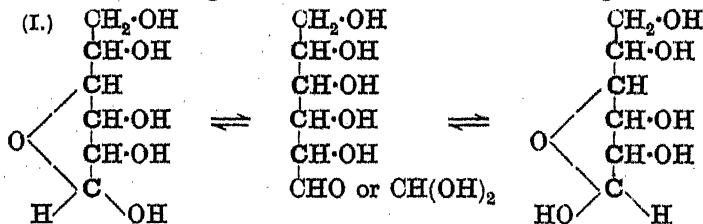
[*] This paper was read on Dec. 20th, 1923, as a verbal reply to the assertion made by Baker, Ingold, and Thorpe at a meeting on Nov. 15th, 1923, that water " does not intervene " in the mutarotation of the sugars. It has been held back for more than a year in order that the reply to their paper (J., 1924, **125**, 268), instead of being merely polemical in character, might be based on new experimental data. Although, therefore, the present paper contains a direct denial of their doctrine of non-intervention, its principal value is to serve as an introduction to a new series of experimental papers, of which the first is printed below.

This scheme, which was first put forward in 1903 by the author of the present paper, was developed in Prof. Armstrong's laboratory at South Kensington in three successive stages as follows :

(i) *The fundamental hypothesis*, that *mutarotation is due to reversible isomeric change*, was suggested for the first time in 1899 in a paper on " Nitrocamphor as an Example of Dynamic Isomerism " (Lowry, J., **75**, 211). Since the mutarotation of nitrocamphor could take place in a large range of organic solvents, and must therefore proceed without any change of composition, it was suggested that the mutarotation of the reducing sugars might be due to a similar *reversible isomeric change**, instead of to the *reversible hydration*, $C_6H_{12}O_6 + H_2O \rightleftharpoons C_6H_{14}O_7$, which E. Fischer (*Ber.*, 1890, **23**, 2326) had postulated on the basis of an analogy with the mutarotation caused by the reversible hydrolysis of gluconolactone, $C_6H_{10}O_6 + H_2O \rightleftharpoons C_6H_{12}O_7$.

(ii) The second step was the identification of the isomeric sugars as the parent compounds of the α- and β-glucosides; this was rendered probable by the observations of Simon in 1901 (*Compt. rend.*, **132**, 407), but was finally established by E. F. Armstrong in 1903 (J., **83**, 1305) by a direct process of hydrolysis by enzymes.

(iii) *The subsidiary hypothesis*, that *the isomeric change of the oxidic sugars proceeds through the intermediate formation of an aldehydic form of the sugar*, which completes the above scheme, was put forward in 1903 (Lowry, J., **83**, 1316) simultaneously with the publication of E. F. Armstrong's paper. This hypothesis was introduced in order to account for the fact that, although a direct interchange of H and OH appears to be impossible in the sugar series, the isomeric change established by Armstrong involves an inversion of sign of *one* of the four $>CH \cdot OH$ groups of the sugar. It was therefore suggested that " the simplest mechanism by which this can be brought about is that which involves the breaking of the γ-oxide ring and the formation of *the aldehyde or its hydrate* as an intermediate product " † (J., 1903, **83**, 1316). In this statement, which was repeated in 1904 (J., **85**, 1565), no distinction was

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* Two isomeric forms of glucose had already been isolated; but their mutarotation was attributed to a complete conversion into a third form of the sugar, the equilibrium mixture being mistaken for a definite compound, just as in the analogous case of π-bromonitrocamphor, of which three forms had been described, one of them being an equilibrium mixture of the other two.

† Baker, Ingold, and Thorpe (J., 1924, **125**, 268) have adopted the former of these alternatives, but have attributed its origin to a German publication of later date. The latter alternative is attacked under the title of " Lowry's hypothesis." It is noteworthy that Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 3195) have quoted the misleading version of my views given by Baker, Ingold, and Thorpe, which they have assumed to be correct, and have ignored my own published statements on the subject.

made between these two forms of the intermediate compound, since either would fulfil equally well the condition, on which the subsidiary hypothesis of an intermediate phase was based, that the optical inversion of the terminal carbon atom must proceed through an intermediate compound in which this atom is no longer asymmetric.

(b) The mechanism by which the intermediate aldehydic sugar is formed was discussed in 1904 (J., 85, 1567), when it was shown that the hydrate, which is the first product of the action of aqueous alcohol on α-glucose, exhibits just the same mutarotation as α-glucose itself,* and cannot therefore be (as Hudson subsequently suggested, J. Amer. Chem. Soc., 1909, 31, 67) the intermediate aldehydrol. An equation was therefore given in which the interconversion of α- and β-glucose in presence of water was represented as depending on a double isomeric change, the two glucoses as well as the intermediate aldehyde being shown as hydrates, as in the following scheme II :

(II.)

$$
\begin{array}{ccc}
\text{CH}_2\cdot\text{OH} & \text{CH}_2\cdot\text{OH} & \text{CH}_2\cdot\text{OH} \\
\text{CH}\cdot\text{OH} & \text{CH}\cdot\text{OH} & \text{CH}\cdot\text{OH} \\
\overset{\text{H}}{\underset{\text{HO}}{>}}\text{O}\!\!<\begin{array}{l}\text{CH} \\ \text{CH}\cdot\text{OH} \\ \text{CH}\cdot\text{OH} \\ \text{C}\end{array} \rightleftharpoons \begin{array}{l}\text{CH}\cdot\text{OH} \\ \text{CH}\cdot\text{OH} \\ \text{CH}\cdot\text{OH} \\ \text{CH(OH)}_2\end{array} \rightleftharpoons \overset{\text{H}}{\underset{\text{HO}}{>}}\text{O}\!\!<\begin{array}{l}\text{CH} \\ \text{CH}\cdot\text{OH} \\ \text{CH}\cdot\text{OH} \\ \text{C}\end{array} \\
\overset{\text{H}}{}\diagup\ \diagdown\text{OH} & & \text{HO}\diagup\ \diagdown\text{H}
\end{array}
$$
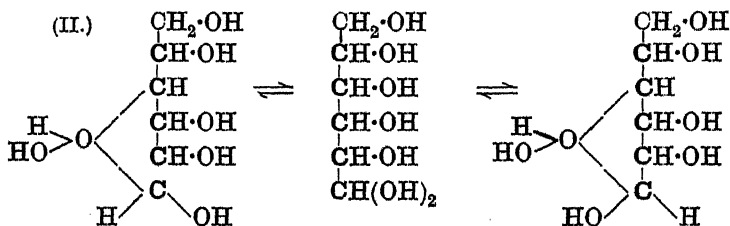
The " reversible hydrolysis " referred to in 1903 (J., 83, 1320) as a possible explanation of the catalysis of glucose by neutral water (in contrast with the inability of chloroform to catalyse the mutarotation of nitrocamphor) and the " hydrocatalysis " referred to in 1904 (J., 85, 1658) must therefore both be interpreted as *an isomeric change consequent upon the addition of water*, since the initial act of hydration is too rapid to produce a mutarotation which can be followed experimentally.†

Before passing away from Scheme II above, it is important to notice that, although other substances may promote isomeric change by forming addition compounds in the manner there suggested, water is unique in that it is the only simple substance which can be

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* Compare Rüiber, *Ber.*, 1922, 55, 3132; 1923, 56, 3185.

† The " hydrate theory " which is attacked by Baker, Ingold, and Thorpe under the designation of " Lowry's hypothesis " is therefore not the one which I developed and described in 1904, but a modification of it which is actually incompatible with my own experimental work, since they assume throughout that the initial process of hydration is the direct cause of the observed changes of rotation, whereas I showed 20 years ago that the initial act of hydration is too rapid to be detected in this way.

added to the aldehydic group of a sugar without destroying its symmetry. In any other type of addition but that represented by the general equation $C_6H_{12}O_6 + R_2O = C_6H_{12}O_5(OR)_2$ the asymmetric character of the terminal carbon atom would be perpetuated, and could only be destroyed by shaking off the catalyst and liberating the free aldehyde, or alternatively by replacing the catalyst by a molecular proportion of water.

(c) In the later editions of Meyer and Jacobson's " Lehrbuch der organischen Chemie," Jacobson and Stelzner cite the aldehydic mechanism, which I put forward in 1903, as an example of a generalised phenomenon which they call " oxo-cyclo-desmotropy." The term desmotropy, which was introduced by Jacobson (*Ber.*, 1887, **20**, 1732; 1888, **21**, 2628) to describe " a rearrangement of bonds consequent upon the displacement of a hydrogen atom," does not here refer (as in the usage suggested by Hantzsch and Hermann) to the possibility of isolating either α- and β-glucose or the intermediate aldehydic form of the sugar, but only to the fact that these isomerides can be transformed into one another by displacing a single hydrogen atom and rearranging the related system of bonds. In adopting this generalisation, Baker, Ingold, and Thorpe (J., 1924, **125**, 268) coupled with it the assertion that water " does not intervene " in the mutarotation of the sugars, and attempted to establish this doctrine by a mathematical argument, based upon the form and spacing of the mutarotation curves, followed by two short series of experiments on the influence of small quantities of added water on the velocity of mutarotation of glucose in methyl alcohol and of tetra-acetylglucose in ethyl acetate. Although these experiments were put forward as " crucial " tests in support of their doctrine of non-intervention, the results are all compatible with a hydrate-mechanism in a system containing (i) sugar, (ii) water, (iii) a hygroscopic solvent, (iv) an unknown catalyst; * they can therefore only be regarded as inconclusive.† There is,

* By working under " clean " conditions, Mr. Owen has been able to arrest completely during a period of 24 hours the mutarotation of a solution of tetra-acetylglucose in ethyl acetate; the mutarotation observed by Baker, Ingold, and Thorpe in dry ethyl acetate was therefore due entirely to catalysis by unknown impurities in their solutions.

† The mathematical calculations for a two-component system are invalid when applied to a three-component system in which the active mass of the water is not the same as its total concentration. This identity might perhaps be assumed in the case of an " ideal " solution, conforming rigidly to Raoult's law of vapour-pressure lowering; but no " ideal solution " is known in which water is one of the components. The presence of a fourth component of unknown origin, character and concentration is even more incompatible with the essential conditions for a crucial test, since if an auxiliary catalyst is necessary, in order to establish the existence of a particular type of curve,

indeed (as in 1904, J., 85, 1566), no valid evidence in the literature to prove that mutarotation can take place except by the intervention of water; * and, since water is known to form a hydrate with the sugar, it would be absurd to suggest that this particular catalyst acts from a distance instead of acting in the normal way by entering into combination with the substance catalysed. In this connexion it is noteworthy that the mutarotation of beryllium benzoylcamphor (which is insoluble in water and forms no hydrates with it, but gives a crystalline addition compound with chloroform) is catalysed by chloroform, although this solvent has been found to inhibit the mutarotation of nitrocamphor, of β-bromonitrocamphor and of tetramethylglucose. This is not likely to be a mere coincidence, and therefore provides strong confirmation of the generally accepted view that one essential property of a catalyst is that it must be able to add on to and split off from the substance catalysed.†

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it should obviously have been added deliberately to materials of which the purity had been established by observing an arrest of mutarotation, instead of being introduced in the form of a casual impurity from the apparatus, solvent or sugar.

In addition to limiting their calculations to two out of four components of the systems studied, the authors impose a drastic limit to the range of concentrations within which they regard it as legitimate to test their doctrine of non-intervention experimentally. Thus, in seeking to prove that the velocity of mutarotation, k, is independent of the concentration, b, of added water, the total concentration of water must not be *too large*, since it is obvious that large additions of water produce large accelerations; and it must not be *too small*, since in the region covered by the phrase " Bakerian dryness " the accelerations produced by traces of water are assumed to be enormous in comparison with their concentrations. There is, however, supposed to be a minute intermediate region, lying below 0·1% of water, in which $dk/db = 0$. The existence of a small " flat " of this kind on the velocity–concentration curve is quite compatible with a hydrate mechanism in a four-component system, which could even give rise to a minimum; but if the experiments quoted as evidence of its existence are examined in the light of the data given in Part XIX below, it will be seen that dk is negligible merely because db also is negligible, and that the " crucial test " is therefore not far removed from the familiar fallacy of supposing that the ratio of two negligible quantities must also be negligible. There is, in fact, with the possible exception of the hitherto unexplored region of Bakerian dryness and purity, no range of concentrations in which the calculated acceleration for 0·1% of water (corresponding with a half-change period of about 3 months) could be detected with certainty by the methods now in use for measuring the velocities of mutarotation.

* The question of alternative catalysts, acting in the same way as water but not containing water, will be discussed fully in a subsequent paper.

† The modern view of the action of catalysts may be summed up by saying that " A catalyst is a reagent which is reproduced as one of the products of the reaction."

2. *Mutarotation dependent on the Intervention of a Catalyst.*

Although attempts to establish the mechanism of chemical changes by dynamical arguments are generally futile (as in the case of hydrolysis, where no conclusive proof has emerged after 50 years of experiment), it is of interest to notice the conclusions to which such arguments lead when viewed in the light of the admissions which were made during the discussion on the present paper, namely (i) that the mutarotation of the sugars in all solvents is dependent on the presence of water, and can be stopped by the removal of water, (ii) that the arrest of mutarotation by drying is easy, and does not require a condition of " Bakerian dryness."

(*a*) If we represent a " tautomeric mechanism," in which water plays no essential part, by the scheme IV,

$$\text{(IV.)} \qquad S_\alpha \rightleftharpoons A \rightleftharpoons S_\beta$$
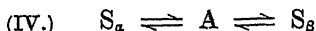
where S_α and S_β represent α- and β-glucose and A is the intermediate aldehyde, we must represent the " hydrate mechanism " which I suggested in 1904 by a similar abbreviation of scheme II above, as follows :

$$\text{(V.)} \qquad S_\alpha \cdot H_2O \rightleftharpoons A \cdot H_2O \rightleftharpoons S_\beta \cdot H_2O.$$
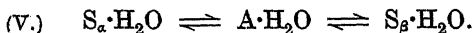
It is then clear that no dynamical analysis can distinguish between the *form* of the mutarotation curves corresponding to schemes IV and V, since in both cases the mutarotation is attributed to two successive isomeric changes.

(*b*) As regards the *spacing* of the curves (*i.e.*, the rate of variation of the velocity of change with the concentration of added water), it is, however, possible to make a comparison of some value between schemes IV and V. Since the hydration of each form of the sugar is a reversible process, the two schemes must be shown in parallel, thus

$$\text{(VI.)} \qquad \begin{array}{ccccc} S_\alpha & \rightleftharpoons & A & \rightleftharpoons & S_\beta \\ \updownarrow & & \updownarrow & & \updownarrow \\ S_\alpha \cdot H_2O & \rightleftharpoons & A \cdot H_2O & \rightleftharpoons & S_\beta \cdot H_2O \end{array}$$
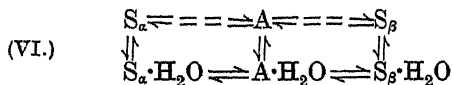
Moreover, since hydration is very rapid, the vertical arrows must be regarded as representing changes which are reversible, but which in practice are almost instantaneous. The proportion of the sugar which is hydrated, as in the lower line of this scheme, can be reduced to zero by careful drying; but it is not certain that it can be increased to 100%, since in the analogous case of gluconic acid the compound becomes partly dehydrated by forming a lactone even in dilute aqueous solutions. We can, however, compare the efficiency of the two mechanisms by noticing the velocity of change (i) in the absence of water, when only the " tautomeric mechanism " is available, and (ii) in aqueous solutions, when the " hydrate

mechanism " is at its maximum efficiency, although still working in parallel with the " tautomeric mechanism," since this cannot be inhibited completely by adding water.   Experiments on these lines show at once that, in the absence of the " hydrate mechanism," the " tautomeric mechanism " produces no " flow " at all from S_α to S_β, whilst quite a rapid flow is produced whenever the " hydrate mechanism " is available.   If, therefore, the question is to be settled by tests of this kind, we must conclude that *the direct interconversion of the anhydrous sugars indicated by the dotted arrows does not in fact take place* and that the only channel which is open from S_α to S_β is the one that passes through $S_\alpha \cdot H_2O$, $A \cdot H_2O$ and $S_\beta \cdot H_2O$.*

(c) It is interesting in this connexion to consider the behaviour of substances in which the asymmetry of the terminal carbon atom would be retained in the intermediate addition compound, as in the alcoholate of an aldehydic sugar, $-CH {<}^{OR}_{OH}$, or the hydrate of an anilino-sugar, $-CH {<}^{OH}_{NHPh}$.   In all such cases the intermediate compound would exist in two forms, which we can call $A_\alpha \cdot H_2O$ and $A_\beta \cdot H_2O$; and, since these can revert only to S_α or to S_β respectively, the channel from S_α to S_β through $A \cdot H_2O$ is now blocked.   Since, however, $A_\alpha \cdot H_2O$ and $A_\beta \cdot H_2O$ are dissociable compounds, inversion can still occur by dissociation to the " symmetrical " compound A, as in scheme VII :

$$\text{(VII.)}\quad A_\alpha \cdot H_2O \rightleftharpoons A + H_2O \rightleftharpoons A_\beta \cdot H_2O.$$
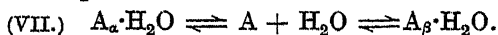
All the arrows shown in the principal scheme VI (except the dotted arrows of the inoperative " tautomeric " mechanism) now represent essential stages in the process, since the whole of the material must now pass through A, as well as through $A \cdot H_2O$ which provides the sole means of access to A; but, if the reversible hydration of the compound A is rapid, the " flow " need not be greatly retarded by this additional stage in the process.   The fact that an anilino-sugar can undergo change only through an anhydrous form of the open-chain compound does not therefore eliminate the necessity for the formation of a hydrate (or of some analogous intermediate addition compound) unless we are to suppose that the isomeric changes of these compounds, unlike those of the parent sugars, do not depend on the presence of water.†

* The possibility of an alternative catalyst acting in the same way as water is again reserved for consideration at a later stage.

† Since the anilino-sugars are stable in presence of alkalis, it is possible that there may be a fundamental difference in the mechanism of the isomeric changes which they undergo, but only in presence of acid catalysts; the experimental data are, however, too scanty for a useful discussion at the present stage.

(d) It will be seen that whilst in 1904 I laid stress on the experimental fact of the formation of hydrates by the mutarotating sugars of which glucose is the type, Jacobson lays stress on the presence of a mobile hydrogen atom in these sugars. It is possible, however, in the light of modern theories of valency, to see that these ideas are not incompatible. Thus, the hydrolysis of an ester was formerly regarded as depending on the formation of an addition compound of the ester with water and the catalyst, thus :

$$[\text{Ester, NaOH, H}_2\text{O}] \text{ or } [\text{Ester, HCl, H}_2\text{O}].$$
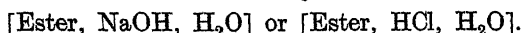
At the present time, however, we should regard the metal in the addition compound as ionised, and assert that it is only the hydroxyl ion of the alkali and not the whole molecule that is really added to the ester; and in a similar way that it is only the hydrogen ion and not the whole molecule of the acid that is added, thus :

$$[\text{Ester, OH, H}_2\text{O}]^-\text{Na}^+ \text{ or } [\text{Ester, H, H}_2\text{O}]^+\text{Cl}^-.$$
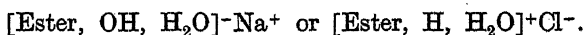
The same treatment can, however, also be applied to the water in this scheme, which provides a hydrogen ion to supplement the hydroxyl ion of the alkali, or a hydroxyl ion to supplement the hydrogen ion of the acid, thus :

$$\left[\text{Ester, OH, H}\right]_{\text{OH}^-}^{\text{Na}^+} \text{ or } \left[\text{Ester, H, OH}\right]_{\text{H}^+}^{\text{Cl}^-}.$$
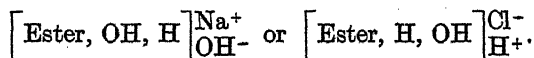
The brackets now contain just the elements that are needed to form the ultimate products of hydrolysis, whilst the ions of the catalyst outside the bracket can be set free to act upon another molecule of the ester.

In precisely the same way, the difference between my hydrate mechanism and Jacobson's desmotropic mechanism appears to depend on nothing more fundamental than the difference between the old view, represented by the equation $\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$, in which the union of ammonia and hydrogen chloride is represented as the formation of an addition compound, and the newer view which regards it as involving only the transfer of a proton from the acid to the base :

$$\text{NH}_3 + \text{HCl} = \overset{+}{\text{NH}}_4 + \overset{-}{\text{Cl}}.$$
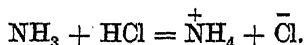
Thus on general grounds we might consider that the mutarotation of an aqueous solution of a sugar in presence of an acid or basic catalyst must involve the formation of an intermediate addition compound of the sugar with the other compounds, thus :

$$[\text{Sugar, NH}_3, \text{H}_2\text{O}] \text{ or } [\text{Sugar, HCl, H}_2\text{O}].$$
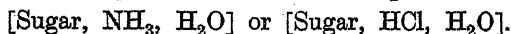
If, however, we adopt the more modern method of formulation, and regard the acid as a proton donator and the base as a proton acceptor, and attribute to the water (as in hydrolysis) a converse

function to that of the catalyst with which it is associated, we can rewrite the schemes which represent the addition of the catalysts to the sugar in such a way as to show only the transference of a proton which is the essential feature of Jacobson's process of desmotropy, thus :

$$\left[\text{Sugar, } -\text{H, } +\text{H} \right] \substack{\text{NH}_4^+ \\ \text{OH}^-} \quad \text{or} \quad \left[\text{Sugar, } +\text{H, } -\text{H} \right] \substack{\text{Cl}^- \\ \text{H}^+}.$$
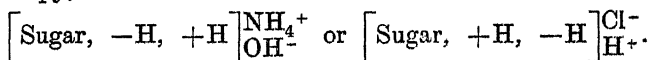
The remainder of this paper is therefore based on the assumption that, since a catalyst is needed in all desmotropic changes, there need be no controversy in reference to the special case of desmotropic change which gives rise to the mutarotation of the sugars. I have therefore worked out, on the basis of the analogy with hydrolysis which is outlined above, a detailed mechanism for the isomeric change of the sugars, and of prototropic compounds generally, on the lines foreshadowed in 1904, but in such a way as also (i) to indicate the important part played by the mobile hydrogen atom, and (ii) to assign a definite function, not only to water, but also to acids and bases, when acting as catalysts for the mutarotation. This detailed mechanism is perhaps incapable of rigid proof, and no crucial tests of its correctness are offered, but it certainly possesses the attributes by which Pasteur claimed to recognise a " true " theory, since it has enabled us to foresee the possibility of a number of important phenomena, which would otherwise have been quite unexpected, but which have since been verified experimentally.

3. The Mechanism of Hydrolysis and Esterification.

On the experimental side, the mutarotation of nitrocamphor and of the sugars shows certain points of resemblance (which it would be unwise to overlook) to the hydrolysis of an ester. Thus, whilst the inversion of sucrose and the hydrolysis of a glucoside are commonly effected with the help of enzymes or of acids, the mutarotation of the reducing sugars, like the hydrolysis of an ester, is accelerated both by acids and by alkalis. Moreover, just as in hydrolysis, alkalis are in general more efficient catalysts than acids. For this reason, the view has been advanced that the reducing sugars are amphoteric, like the esters, the dissociation constant of the sugar as an acid ($K_a = 10.5 \times 10^{-13}$ for glucose at 25°) * being much larger than its dissociation constant as a base ($K_b = 7.8 \times 10^{-17}$ at 25°; Kuhn and Jacob, Z. physikal. Chem., 1924, 113, 395).

The intermediate compounds formed by combination with acidic and basic catalysts do not appear to have been isolated in the case of the reducing sugars, with the exception of certain com-

* Euler, Myrbäch, and Rudberg (Arkiv Kemi, Min. Geol., 1923, 8, No. 28) give $K_a = 0.12$, 0.31, 0.71×10^{-14} at 0°, 10°, and 20°.

pounds of the aldehyde-ammonia type; * but in the case of the esters, where a larger range of materials is available, this has been done in certain instances. Thus an addition compound of sodium methoxide with ethyl benzoate has been isolated by von Pechmann (*Ber.*, 1898, **31**, 503); and an unstable addition compound of ethyl acetate with hydrogen bromide, m. p. − 36°, has been isolated by Maass and McIntosh (*J. Amer. Chem. Soc.*, 1912, **34**, 1272). The electronic theory of valency requires, however, that all these addition compounds must be formulated as " salts," held together by the electrostatic attraction of oppositely charged ions and not by real bonds, since any process of electron sharing would at once create a surplus of electrons. The initial addition compounds of methyl acetate with sodium hydroxide and with hydrogen chloride may therefore be written as follows :

$$\overset{\overset{-}{O}\,\overset{+}{Na}}{\underset{\underset{OH}{|}}{CH_3 \cdot C}} - O \cdot CH_3 \qquad \text{and} \qquad \overset{O\quad \overset{-}{Cl}}{\underset{\underset{H}{|}}{CH_3 \cdot C} - \overset{+}{O} \cdot CH_3}$$

<div align="center">Oxy-salt.   Oxonium salt.</div>
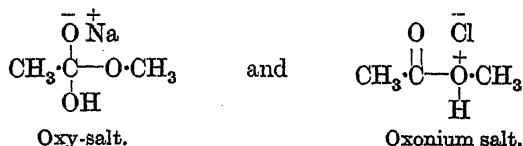
If the free ions are omitted, the complexes formed by the combination of the ester with the hydroxyl or hydrogen ion of the catalyst may be formulated as follows :

$$\overset{\overset{-}{O}}{\underset{\underset{OH}{|}}{CH_3 \cdot C}} - O \cdot CH_3 \qquad \text{and} \qquad \overset{O}{\underset{\underset{H}{|}}{CH_3 \cdot C} - \overset{+}{O} \cdot CH_3}$$
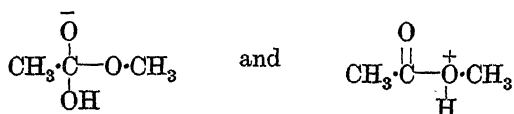
In these complexes hydroxyl and hydrogen, supplied by the catalyst in the form of ions, are now represented as neutral radicals, joined to the ester by real bonds, their electric charges having been transferred to the oxygen atoms of the ester.

Mere salt formation, however, is not sufficient to produce hydrolysis, which by definition demands the addition of a molecule of water. This can be represented as adding on to the oxygen atom which still remains unoccupied in the above formulæ, thus :

$$\overset{\overset{-}{O}\overset{+}{Na}\;\overset{-}{O}H}{\underset{\underset{OH\;\;H}{|\quad\;\;|}}{CH_3 \cdot C}---\overset{+}{O} \cdot CH_3} \qquad \text{and} \qquad \overset{\overset{-}{O}H\;\overset{+}{}\;\overset{-}{Cl}}{\underset{\underset{OH\;\;H}{|\quad\;\;|}}{CH_3 \cdot C}---\overset{+}{O} \cdot CH_3}$$
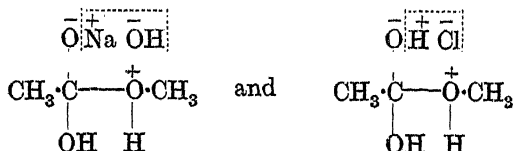
* Lobry de Bruyn, *Rec. trav. chim.*, 1893, **12**, 286; 1895, **14**, 134; 1899, **18**, 72; Ling, J., 1922, **121**, 1384; *J. Soc. Chem. Ind.*, 1922, **41**, 151. Compare also the addition compounds with guanidine (Morrell and Bellars, J., 1907, **91**, 1010).

If the free ions associated with the complex are again neglected, it will be seen (i) that the hydrolysis of an ester both by alkaline and by acid catalysts proceeds by the addition to the ester of hydrogen and hydroxyl radicals which are supplied to it in the form of ions; (ii) that whilst one of these ions is derived from the catalyst, the water provides either hydrogen ions to supplement the hydroxyl ions of an alkaline catalyst, or hydroxyl ions to supplement the hydrogen ions of an acid catalyst, and (iii) that this addition gives rise in each case to the same bipolar molecule (or " Zwitterion "), which is shown as an intermediate product in the following scheme :

$$CH_3 \cdot CO \cdot O \cdot CH_3 \rightleftharpoons CH_3 \cdot \overset{\bar{O}}{\underset{OH}{C}} \overset{+}{\underset{H}{O}} \cdot CH_3 \rightleftharpoons$$

$$CH_3 \cdot \overset{\bar{O}}{\underset{OH}{C}} \equiv O \cdot CH_3 \rightleftharpoons CH_3 \cdot \overset{O}{\underset{OH}{C}} + HO \cdot CH_3$$
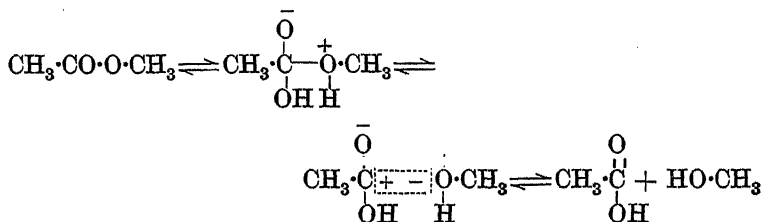
In this scheme, the hydrolysis of an ester is formulated, like the hydrocatalysis of glucose, as an " isomeric change following the addition of water "; but the " isomeric change " now takes the form of a fission of the molecule by the rupture of a bond, the final ionisation of which provides the electric charges which are needed to neutralise those already present in the " Zwitterion."

The reverse process of esterification, which is of interest in connexion with the reconversion of the aldehydic form of a sugar into the stereoisomeric oxides, only takes place in presence of *acid* catalysts. It may be formulated in a converse way as depending on the formation of an addition compound of the acid and alcohol with the catalyst, followed by the removal of a molecule of water and the liberation of the catalyst from the complex. The condensation of the alcohol and acid therefore appears to involve (i) the repression of the ionisation of the organic *acid*, with a development of its ketonic functions (J., 1923, **123**, 827), (ii) the addition of a proton to the *alcohol* (compare Goldschmidt and Udny, *Z. physikal. Chem.*, 1907, **60**, 728), thereby giving to the alcohol the proton-donating functions of an acid,*

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* Compare the view that aqueous acids are really oxonium salts, containing oxonium ions and not free protons, the separation of which has been formulated as an endothermic action involving the absorption of 262,000 calories (Fajans, *Ber. phys. Ges.*, 1919, **21**, 709). If this estimate is even approximately correct, it is evident that, not only must the ionisation of an acid be formulated as a double decomposition, $H_2O + HCl \rightleftharpoons \overset{+}{H_3O} + \bar{Cl}$, and not as a dissociation, $HCl \rightleftharpoons \overset{+}{H} + \bar{Cl}$, but that physical chemists have made

(iii) the co-ordination of the proton of this complex with the carbonyl oxygen of the acid (compare Pfeiffer, *Annalen*, 1913, 398, 152) as a preliminary to (iv) the addition of the proton-donating complex of the alcohol to the carbonyl group of the acid, according to the normal rules for the addition of a hydride such as HCN to an aldehyde or ketone, (v) the elimination of the proton of the catalyst, and of a molecule of water, from the intermediate condensation product.

$$CH_3 \cdot CO_2H + \overset{+}{H} + HO \cdot CH_3 \rightleftharpoons CH_3 \cdot C \overset{O \text{---} \overset{+}{H}}{\underset{OH \ H}{<}} O \cdot CH_3$$

$$\rightleftharpoons CH_3 \cdot \underset{\underset{OH \ H}{|}}{\overset{\overset{OH}{|}}{C}} \overset{+}{O} \cdot CH_3 \rightleftharpoons CH_3 \cdot C \overset{O}{\underset{O \cdot CH_3}{<}} + \overset{+}{H} + H_2O$$
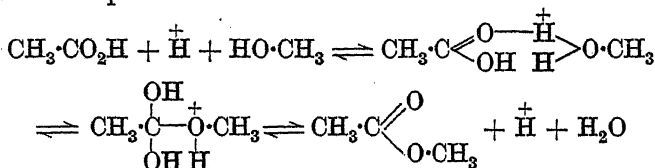
4. *Prototropy* * *as an Intermolecular Process of Addition and Removal of a Proton.*

The fact that water as well as alkali or acid is needed for hydrolysis scarcely needs demonstrating, but when dealing with isomeric changes the function of water as a promoter of chemical action is less obvious. Here again, however, just as in the case of hydrolysis, there is an instructive contrast between two principal groups of cases, since the *ionotropic changes* of the aromatic series, *e.g.*, $C_6H_5 \cdot NHCl \longrightarrow C_6H_4Cl \cdot NH_2$, which involve the migration of other ions as well as of a proton, are catalysed only by acids, like the inversion of sucrose, whilst *prototropic changes*, which involve only the migration of a proton, are catalysed both by acids and by alkalis, like the hydrolysis of an ester.

It must, however, be remembered that prototropic change cannot be regarded as a mere jumping of a proton from one point to another *within the molecule*, as in the old theory of tautomerism, but must be represented as an intermolecular action, which depends (like so

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a mistake in formulating the ionisation of water as $H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{OH}$, since this action also should be regarded as a transfer of protons, $2H_2O \rightleftharpoons \overset{+}{H_3}O + \overset{-}{OH}$ (compare the redistribution of protons in the balanced action $CO_2 + 2NH_3 \rightleftharpoons NH_2 \cdot CO \cdot O \cdot NH_4$) instead of as a simple dissociation into hydrogen and hydroxyl ions.

* It has been suggested that the transfer of a proton would be described more accurately as " protonotropy." In the present paper the shorter form suggested in 1923 (J., 123, 828) has been retained provisionally, on the ground that the " n " of the word proton, although convenient as a mnemonic, is not essential to the definition. The longer form is, however, attractive on account of its more fully descriptive character, and might be allowed to take the place of the shorter form if it should prove in practice to be more acceptable.

many other chemical changes *) on the presence of molecules of other kinds, and may therefore be suspended if these are not present in the system. In particular, all prototropic changes appear to involve two distinct † chemical processes, as follows : (i) the removal of a proton from one part of a molecule to some outside basic or proton-accepting component of the system, and (ii) the addition to another part of the molecule of a proton, also derived from outside, namely, from some acidic or proton-donating component of the system. Moreover, a base which is very efficient in removing a proton from the organic molecule will be correspondingly reluctant to part with the proton that is required to reconvert the organic ion into a neutral molecule ; and an acid which is ready to supply a proton to the organic ion will tend to repress the equally essential removal of a proton from the organic molecule. Whilst, therefore, prototropic changes are catalysed both by acids and by bases, we might anticipate that a base would be most efficient when water is also present to act (like a weak acid) as a source of protons for the organic ion, and in the same way that an acid might be most efficient when water is added to act (like a weak base) as an acceptor of protons from the isomeric hydrides. The experimental verification of this prediction, which follows naturally from the mechanism described above (but which could certainly not be deduced from the dictum that " the mode of action of catalysts is quite unknown ") is summarised in Part XIX below ; but it is also being used as a basis for the further extended investigation which the importance of the observations demands.

5. *Mechanism of Isomeric Change in the Reducing Sugars.*

The chemical changes involved in the interconversion of α- and β-glucose through the intermediate formation of the aldehydic form of the sugar are intermediate in character between those described in §§ 3 and 4 above, since (i) *the breaking of the ring in the oxidic sugars involves the rupture of a carbon–oxygen bond*, just as in the hydrolysis of an ester or of Fischer's mutarotating gluconolactone, but (ii) *the formation of the aldehyde is not accompanied by a change of composition*, so that, even when the change is determined by the action of water, this action must be classed as a hydrocatalysis and not as a simple hydrolysis. Further investigation shows, however, a very close analogy between the hydrolysis of gluconolactone and the hydrocatalysis of glucose. Thus, on the

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* It is probable that the only real intramolecular changes are those of the radioactive type, in which *even the other atoms in the same molecule* do not intervene to accelerate or retard the action.

† These changes may, however, occur simultaneously in the same electric circuit, as in Armstrong's electrolytic theory of chemical change.

one hand, the same basic C–O–C group is available in both compounds to provide a point of attachment for acid catalysts or for water. On the other hand, the carbonyl group, which forms the natural point of attachment for bases, both in the case of the esters and of gluconolactone, has now been reduced, $>C{=}O \rightleftharpoons >CH{\cdot}OH$, but without losing its acidic properties, since bases can now act by removing the proton (shown in italics in the preceding formula) which is eliminated in the formation of glucosides, instead of by adding on a hydroxyl ion. The initial stage in the conversion of the oxidic into the aldehydic form of the sugar can therefore be formulated as depending on the combination of the sugar either with *base plus water* or with *acid plus water* * as in the following scheme : †
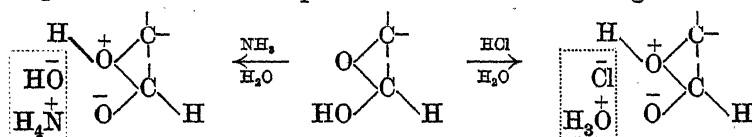
It can then be seen (i) that (just as in hydrolysis) the initial products formed by basic and acid catalysts are salts of the same bipolar molecule, differing only in the nature of the two " free ions " with which the " bound ions " of this complex are associated,‡ (ii) that in this bipolar molecule the hydroxylic and the aldehydic group of the final product are already in existence, although still joined by a bond which is now superfluous, (iii) that the ionisation of this bond can, however, provide just the right electric charges for neutralising those on the bipolar molecule. The whole process of isomeric change can therefore be expressed in a simplified scheme, from which the ions of the catalyst are omitted, as follows :
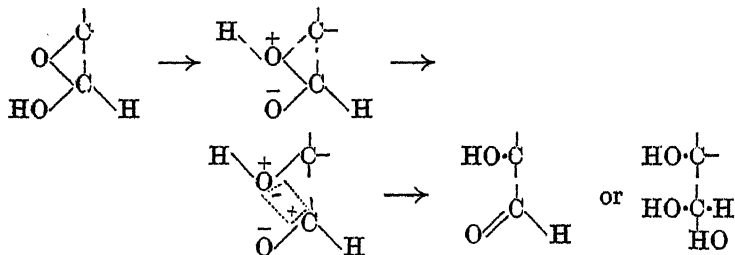
* The question of mutarotation in isoelectric solutions will be discussed in a later paper.

† In this scheme, the intermediate atoms of carbon in the γ-oxide ring are omitted.

‡ The bipolar molecule can scarcely be expected to exist except in the form of a salt (or of a hydrate if water plays the part of the acid and base). The extent to which it is formed, and the velocity of the chemical changes in which it is concerned, will therefore depend on the strength of the acid or base with which it is combined.

In the final stage of this scheme both of the alternative products are shown, namely, the *aldehyde*, which is produced if the electric charges of the ionised carbonyl group are neutralised by forming a double bond, and the *hydrate*, which is produced when these charges are neutralised by adding on the ions of water.

6. *Conclusions.*

The mechanism set out in § 5 above is put forward as a natural development, in view of the clearer conceptions of the electronic theory of valency, (i) of the fundamental hypothesis (J., 1899, **75**, 213) that the mutarotation of the sugars is due to a reversible isomeric change, and (ii) of the subsidiary hypothesis (J., 1903, **83**, 1316) that this change proceeds through an intermediate aldehydic phase; it also embodies (iii) E. F. Armstrong's "oxonium" formula for the hydrate of α-glucose (J., 1903, **83**, 1309) and (iv) the formulation of hydrolysis as an isomeric change following the addition of water (J., 1904, **85**, 1567). It appears to cover all the essential points raised by Baker, Ingold, and Thorpe, but goes beyond the point that was reached in our 1899 or in their 1924 paper, in that it not merely attributes mutarotation to isomeric change, but also assigns a definite part to those chemical agents without which, it appears, mutarotation cannot proceed. In this way, it removes some of the vagueness which attaches to the use of the terms "tautomerism" and "catalysis" in connexion with the phenomena of mutarotation, since these terms have served hitherto mainly as a cloak to conceal our ignorance of the method of action of these essential chemical agents, although their importance has long been obvious.

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CLXXXIX.—*Studies of Dynamic Isomerism. Part XIX. Experiments on the Arrest of Mutarotation of Tetramethylglucose.*

By THOMAS MARTIN LOWRY and EVAN MATTHEW RICHARDS.

1. *Classification of Solvents.*

The mechanism described in Part XVIII (preceding paper) leads to the conclusion that it should be possible to divide solvents into three groups as regards their behaviour towards prototropic changes, such as those which give rise to the mutarotation of the sugars, thus :

(i) The first group should include all those solvents which can receive a proton from the compound or give a proton to its ion. These amphoteric solvents should act as *complete catalysts* for the mutarotation.

(ii) The second group should include solvents which possess either basic or acidic properties, but not both. Solvents of this group may be unable to act as complete catalysts when used alone, but may become very efficient when used as one component of a *mixed catalyst*.

(iii) The third group should include solvents which possess neither basic nor acidic properties, and which may therefore be expected to possess no catalytic properties for this particular type of isomeric change.

In the paper in which the mutarotation of nitrocamphor was first described, organic solvents were divided into two groups as follows.* " In solvents containing oxygen, such as the alcohols, acids, ethers and ethereal salts, equilibrium is reached on the average in about four hours at 15°. The hydrocarbons and compounds such as chloroform and carbon disulphide are much less active, and a period of from two days to a week or more is required before equilibrium is reached in these solvents " (J., 1899, **75**, 219). The view was also advanced that " From certain observations that have been made with chloroform solutions, it seems doubtful whether the second group of solvents are capable by themselves of bringing about the isomeric change at all." The occasional arrest of mutarotation in solutions of nitrocamphor in *chloroform* was, indeed, clear proof that the isomeric change was not spontaneous, and could not proceed in the absence of a catalyst; but it was not until 10 years later (J., 1908, **93**, 119) that the discovery of the anticatalytic action of carbonyl chloride made it possible to repeat the observation of arrested mutarotation in two other solvents, namely *benzene* and *ether*, and thus to eliminate them from the category of " complete catalysts " for the mutarotation of nitrocamphor. The experiments on ether showed, moreover, that the presence of oxygen in the molecule was not the criterion of a complete catalyst, a conclusion that was afterwards confirmed by the experiments of Irvine and Scott (J., 1913, **103**, 584), in which the mutarotation of one of the dimethylglucoses was " suspended " for about a fortnight in a solution in *acetone*. There can therefore be little doubt that the real criterion for catalytic activity must be the possession of acid or basic properties as suggested in Part XVIII. This view has already been made the

* The same classification was adopted four years later by Stobbe (*Annalen*, 1903, **326**, 347) in connexion with keto-enolic changes.

basis of several series of new experiments (some of which are described below) and these have in every case given results which are in harmony with the mechanism now under examination.

2. Discussion of Experimental Results.

In the present paper the evidence as to the conditions under which mutarotation can take place has been extended in two directions (i) by repeating with a suitable sugar the observations which led to the original discovery of arrested mutarotation in nitrocamphor, (ii) by examining a number of additional solvents in which arrested mutarotation had not been observed previously either with nitrocamphor or with a sugar. The sugar selected was tetramethylglucose, the mutarotation of which was recorded by Purdie and Irvine in 1904 (J., **85**, 1049). Whereas glucose has been found to be quite unsuitable for experiments which depend on the use of carefully purified materials, tetramethylglucose has proved to be an ideal sugar for the purpose. The different behaviour of the two sugars cannot be attributed to any difference in their reactivity, or to a greater sensitiveness of glucose to the influence of catalysts, since their velocities of mutarotation are almost identical, except in the case of the low velocities which are recorded when attempts are being made to arrest the mutarotation completely by careful purification. The difference is therefore probably due to the fact that glucose can be crystallised only from water or from water-soluble solvents, under conditions which permit (and generally favour) contamination with water-soluble impurities. Tetramethylglucose, on the other hand, crystallises excellently from solvents such as light petroleum,* which not only tend to separate water-soluble impurities from the sugar, but can themselves be dried and purified by the most drastic processes.

(a) *Benzene and Chloroform.* The experiments varied very greatly in difficulty. It was found that the mutarotation in

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* The tetramethylglucose used by us had been crystallised from light petroleum, boiling below 40°. When heated quickly, it melted at 88° (Purdie and Irvine give 88—89°), but when heated slowly it began to melt at 80°; the latter temperature may therefore be taken as the " equilibrium temperature " (Lowry, J., 1899, **75**, 233), or the "natural freezing point" (Findlay, " Phase Rule," 1923, p. 158) of the equilibrium mixture. On the assumption that the dispersion ratio a_{5893}/a_{5461} has the usual value 0·85 of the sugar series, the rotatory powers may be compared with those given by Purdie and Irvine as follows :

	In benzene.		In water.	
L and R : $[a]_{5461}$	129°——→103°		117°——→ 95°	
L and R : $[a]_{5893}$	109°——→ 88°		100°——→ 81°	
P and I : $[a]_{5893}$	111°——→ 85°		102°——→ 83°	

benzene was very difficult indeed to arrest, a result that is in accordance with the view expressed in an earlier paper (J., 1904, **85**, 1566) that " although the proportion of water . . . may be small, the whole of it is available for hydrolysis," whereas in hygroscopic solvents " the activity of the water is greatly lessened by combination with the solvent." Similar difficulties would no doubt have been experienced in the case of *chloroform*, but for the fact that some samples happen to contain the right amount of carbonyl chloride to serve as an anti-catalyst for the more active impurities in the solution; we were therefore able, although only on one occasion, to observe in this solvent a particularly long arrest of mutarotation, extending over a period of about 10 days.

(b) *Ethyl Acetate.* The experiments on *ethyl acetate* were of special interest in view of the fact that Baker, Ingold, and Thorpe (J., 1924, **125**, 268) recorded a finite velocity of mutarotation for solutions of tetra-acetylglucose in dry ethyl acetate. Our experiments showed, however, that the mutarotation of tetramethylglucose in this solvent could be arrested completely during a period of several hours, although nothing of the sort was observed when glucose was used instead of the methylated sugar. Moreover, a preliminary experiment with a small sample of tetra-acetylglucose gave (with the help of a new technique) an exceptionally perfect arrest, during a period of about 24 hours. There can therefore be no doubt that ethyl acetate is not a catalyst for the mutarotation of the sugars, and that the finite velocities of mutarotation hitherto recorded have been due to the use of impure materials or to accidental contamination of the solutions.

(c) *Water and the Alcohols.* No such conclusive evidence is available as yet in the case of the alcohols. Irvine and Hogg (J., 1914, **105**, 1390) record that " when special precautions are adopted to secure the absence of catalysts, the mutarotation of monomethylglucose in methyl alcohol is so slow that the transformation $\alpha \rightleftharpoons \beta$ remains practically suspended "; but their numerical data show that the mutarotation, although " exceedingly slow," was of the same order as in the experiments with tetramethylglucose which are described below. Baker, Ingold, and Thorpe also record a finite velocity of mutarotation for solutions of glucose in dry methyl alcohol. Since none of the attempts made hitherto to arrest the mutarotation of a simple sugar * in methyl alcohol has been completely successful, it is only possible to conclude that methyl alcohol *may* be a complete catalyst, in

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* Irvine and Hogg's experiments on monomethylglucoseanilide, in which mutarotation was observed only in presence of acids, will be discussed in a

virtue of its weak amphoteric properties, but that its efficiency as a catalyst is not greater than 3% of that of water.

Ethyl alcohol gives the same kind of ambiguous results as methyl alcohol, so that at the present time *water* is the only solvent of which we can assert definitely that it can act as a complete catalyst for the mutarotation of the sugars. The original proof that the catalytic activity of water does not depend on acid or basic impurities in the solvent or sugar was given in the first paper of this series (J., 1903, **83**, 1314); but the later quantitative studies of Osaka (*Z. physikal. Chem.*, 1900, **35**, 661), Hudson (*J. Amer. Chem. Soc.*, 1907, **29**, 1572), Euler (*Biochem. Z.*, 1920, **107**, 150; *Arkiv. Kem., Min. Geol.*, 1923, **8**, No. 28), and Kuhn and Jacob (*Z. physikal. Chem.*, 1924, **113**, 389) have confirmed this early view by showing that whilst the velocity of mutarotation passes through a minimum at an isoelectric point in slightly acid solutions ($p_H = 5$), it is not reduced to zero. There is, however, no justification as yet for asserting that water is the *only* complete catalyst for mutarotation, since there is no reason why the search for alternative catalytic solvents should not meet with the same success as the search for other ionising solvents for use as alternatives to water in electrolysis.

(*d*) Apart from water and aqueous alcohols, the only common solvents in which glucose dissolves freely are formamide and pyridine. The mutarotation of glucose in pyridine was first observed by Behrend and Roth in 1904 (*Annalen*, **331**, 361). The mutarotation was rapid, passing to completion during the first night *at a temperature of* 0°; if, therefore, these observations had been available when the classification of solvents into two groups was first suggested, there can be little doubt that pyridine would have been included with the oxygenated compounds in the *active* group of solvents. This conclusion would also have appeared inevitable in view of the well-known catalytic activity of bases in the mutarotation of aqueous solutions of glucose (O'Sullivan and Thompson, J., 1890, **57**; compare J., 1903, **83**, 1314), as well as of nitrocamphor in non-aqueous solutions (J., 1899, **75**, 221; 1908, **93**, 107). The statement that glucose undergoes mutarotation in pyridine has indeed been accepted without question during a period of 20 years, and has been quoted as valid evidence, first against Fischer's theory of hydrolysis as the cause of mutarotation, and then against the theory of hydrocatalysis. It is now shown to rest on no valid foundation of fact, since the minute residual velocity of mutarotation which was exhibited by solutions of glucose in dry pyridine disappeared completely in the case of tetramethylglucose, which gave a well-marked period of induction before mutarotation began to take place. Pyridine is therefore

the first clearly defined example of a substance which has no catalytic properties of its own for the mutarotation of the sugars, but which becomes extremely efficient when used as one constituent of a mixed catalyst. The discovery of this new type of catalyst may be regarded as a decisive vindication of the mechanism by which alone the attempt to arrest the mutarotation of a sugar in presence of a base was rendered a plausible proposition.

3. *Chloroform a Solvent but not a Catalyst.*

In the first experiment, a 4% solution of tetramethylglucose in a " pure " chloroform prepared by the United Alkali Company gave a fairly rapid mutarotation from $a = 9·07°$ (initial) to $8·51°$ (final) in a 2-dcm. tube, in spite of the fact that a silica polarimeter tube was used. In a second experiment, however, an " arrest " of mutarotation was observed by using a 4% solution of tetramethylglucose in medicinal chloroform (containing alcohol), which had been purified by shaking three times with sulphuric acid and distilled. The part of the solution which was transferred to the silica polarimeter tube gave the following readings :

Time (days)	1	2	3	4	5	6	7	8	9	10
a_{5461} =	9·06°	9·02°	9·02°	8·96°	8·96°	9·01°	9·01°	9·07°	9·07°	9·08°

The temperature of the tube was kept at 20° for the first 120 hours, but the circulation of water at this temperature was stopped during the nights following the fifth day, although all the readings were still taken at 20°. At the end of a week, a few drops of the solution were added to make up for leakage or evaporation; the rotatory power of the solution in the tube may therefore have been increased slightly as the result of a slow evaporation of the volatile solvent, but this would not be sufficient to account for the arrest of mutarotation, since of half a dozen attempts to produce this effect only one was successful. The rotatory power of the remainder of the solution, which had been kept in a glass flask in a thermostat at 20°, had fallen at the end of 13 days about halfway towards the usual final value, the reading corresponding to those given above being $a = 8·74°$.

The arrest of isomeric change in chloroform cannot be attributed either to excessive purification or to intensive drying. In particular, since the polarimeter tube could not be ignited, and was only dried by drawing air through it whilst still warm from prolonged steaming, the arrest of mutarotation could not be due to any approach to Bakerian dryness; moreover, minute traces of water were actually added on the eighth and ninth days, without initiating any rapid change. Traces of carbonyl chloride would, however,

not only remove bases in the form of carbamides, but would also replace small amounts of water by anhydrous hydrogen chloride, a compound which does not behave as an acid, and is probably not a catalyst, when water is not present (compare Soper, J., 1924, **125**, 768). In the same way, the addition of a drop of pyridine at the end of 10 days did not produce any immediate mutarotation, probably because, in the absence of water, the catalytic properties of this compound also are insignificant; but the addition of pyridine caused the solution to become cloudy and the observations were therefore discontinued.

4. Experiments with Benzene.

In the case of nitrocamphor it was shown in 1908 (J., **93**, 119) that, by working in silica vessels and in presence of traces of carbonyl chloride, the velocity of mutarotation in benzene could be reduced in the ratio of 125 : 1, from 0·0001 to 0·0000008, whilst the velocity in ether was reduced in the ratio of 50 : 1 from 0·0015 to 0·000026. The view was therefore expressed that " there can be little doubt that in ether, as in benzene and chloroform, the isomeric change is not spontaneous, but depends on the presence of impurities." No fresh experiments have been made in order to determine the behaviour of *ether* towards the sugars, but a new series of experiments has been made with solutions of tetramethyl-glucose in *benzene* as follows : (i) Commercial benzene was shaken repeatedly with sulphuric acid to remove thiophen, washed with aqueous sodium carbonate, dried over calcium chloride, frozen and drained until its freezing point was constant, stored for 18 months over sodium wire, distilled from phosphoric oxide in a glass flask which had been filled with concentrated sulphuric acid during a period of 6 months, and was finally collected (without using a condenser) in a silica flask cooled in ice covered with liquid paraffin. In spite (or because) of this careful purification, and of the fact that the solution was made up in a silica flask, and examined in a well-steamed silica tube, the mutarotation in *dry* benzene was complete within about 2 days, the period of half-change being 14 hours, and the velocity coefficient about 0·00086. In *wet* benzene, which had stood over water for 3 months, the mutarotation during the first day was about twice as fast as in dry benzene, with a velocity coefficient of 0·0016; but during the night the action proceeded more slowly, although the pump attached to the thermostat was left working, with the result that the average velocity was rather less than in the experiment with dry benzene. It therefore appeared possible that prolonged contact with water, by extracting water-soluble impurities from the benzene, had dimin-

ished its catalytic properties to approximately the same extent as prolonged drying by contact with sodium.

(ii) The attempt to clean the polarimeter tube by steaming was then suspended, since the tube appeared to be purified more effectively by repeated use with clean solvents. The silica tube with the best record was, therefore, merely rinsed with dry benzene, without even removing the end-plates. As a result, the velocity coefficient of a sample of tetramethylglucose, which had been dried by standing over sulphuric acid in a vacuum for 4 days, fell to one-eighth of the value formerly recorded, as is shown in Table I.

TABLE I.

Mutarotation of Tetramethylglucose in Dry Benzene.

(4% Solution by volume made up in a silica bottle, and examined in a 2-dcm. silica polarimeter tube at 20°.)

Time.	α_{5461}	$k \times 10^3$.*	Time.	α_{5461}.	$k \times 10^3$.
12 mins.	10·32		7 days	9·08°	0·09
24 ,,	10·32		8 ,,	9·02	0·09
3 hours	10·33		9 ,,	8·93	0·09
18½ ,,	10·09	0·10	11 ,,	8·82	0·08
26¼ ,,	10·00	0·11	13 ,,	8·79	0·07
46¾ ,,	9·81	0·11			
54½ ,,	9·68	0·11	‡307 hours	8·79	
65½ ,,	9·57	0·11	308½ ,,	8·35	18
90½ ,,	9·44	0·10	309 ,,	8·33	17
98 ,,	9·40	0·10	310 ,,	8·30	
114½ ,,	9·29	0·10	311½ ,,	8·26	
122 ,,	9·25	0·10	314 ,,	8·26	8·26
138½ ,,	9·18	0·10	317½ ,,	8·28	
†147 ,,	9·14	0·10	330 ,,	8·24	

$$k = 0·00010. \qquad \text{Half-change period (obs.)} = 114 \text{ hours.}$$

* $k = 1/t \cdot \{\log (a_0 - a_\infty) - \log (a_t - a_\infty)\}$. In calculating this coefficient the time was always expressed in *minutes*.

† At this stage the circulating water was stopped during the night-time, so that the average temperature of mutarotation was below 20°, although all the rotatory powers were read at this temperature.

‡ At 307 hours a trace of water was added to the solution in the tube; and from this time to the end the circulation of water at 20° was maintained continuously.

During the first 6 days the velocity coefficient was very steady at 0·0010, corresponding to a half-change period of 114 hours; after that, the circulation of water from the thermostat was maintained only during the day, and the velocity coefficient was therefore diminished slightly as a result of cooling during the night. After 13 days, a drop of water was added and the temperature was then maintained at 20° until mutarotation was complete. In this case *the addition of water increased the velocity of mutarotation more than* 100-*fold*. This result was in striking contrast to the failure of a much smaller quantity of added water to initiate a rapid

mutarotation in a solution of the same sugar in chloroform. The difference may be accounted for in part by the protective influence of carbonyl chloride in the chloroform; but since the fall of rotatory power after the addition of water was more rapid than in the case of samples of benzene which had been saturated by standing over water, the results here recorded can be explained most easily by supposing that the " dry " benzene already contained some substance which was potentially a catalyst, but which developed its catalytic activity only on the addition of water. This conclusion is in agreement with that already reached in paragraph (i) above, in comparing the behaviour of wet and dry benzene.

(iii) Subsequent experiments with wet benzene gave irregular values for the velocity coefficient, e.g., 0·0003, 0·0008, 0·0005, and 0·0011, the first and fourth of these values being given by solutions of tetramethylglucose in benzene saturated with water, whilst the second and third were for mixtures of equal volumes of wet and dry benzene; but in no case was the velocity of mutarotation as low as that recorded for dry benzene in (ii) above.

The observations described under (i) to (iii) above can only be explained by applying to the sugars the view, already expressed in the case of nitrocamphor, that pure benzene has no appreciable catalytic properties of its own, but may acquire them by the addition of impurities. These impurities, however, must include other substances beside water, since the catalytic activity of wet benzene is not constant (like that of water or of the more aqueous mixtures of water and alcohol), but varies over a very wide range. Thus the lowest velocity recorded for a solution in wet benzene was only one-fortieth of the velocity in water; but in three other cases, in which equal care was taken to avoid contamination, velocities two, three, and four times as great as this minimum were observed; and in the one instance cited in paragraph (ii) above the velocity was of the same order as in water.

5. Ethyl Acetate not a Complete Catalyst.

(a) Experiments with " dry " ethyl acetate. The solvent was purified in the usual way with sodium carbonate and calcium chloride, and dried by distilling twice from phosphorus pentoxide. The readings in Table II (a) show that the rotatory power was steady within ± 0·02° during a period of about a day and that mutarotation then proceeded with increasing velocity, but always quite slowly, during a period of about a week, after which the main series of observations was stopped. At the end of this time, however, the rotatory power had only fallen by 0·2° on a total of about 3°. Moreover, the subsequent mutarotation was so slow

that, when a second sample of the solution was transferred after 48 days from the silica flask to a silica polarimeter tube, the action was found to be still incomplete. The transference of the second sample from the flask to the tube was, however, followed during the next 3 days by a more rapid mutarotation at the rate of about 0·1° per day. The early readings are shown graphically in Fig. 1, together with data for a solution in wet ethyl acetate.

TABLE II.

Mutarotation of Tetramethylglucose in Ethyl Acetate.

(4 g. in 100 c.c. examined in 2-dcm. silica polarimeter tubes at 20°.)

(a) Dried.		(b) With 2·42% of water.		
Time.	a_{5461}.	Time.	a_{5461}.	k (min.).
¼ hour	9·78°	½ hour	9·88°	—
1 ,,	9·80	1 ,,	9·88	—
2 hours	9·80	2¼ hours	9·82	—
3½ ,,	9·79	4 ,,	9·82	0·00009
5 ,,	9·80	5 ,,	9·80	0·00009
7 ,,	9·81	6 ,,	9·80	0·00009
8 ,,	9·80	7 ,,	9·78	0·00009
10½ ,,	9·81	9½ ,,	9·71	0·00011
23 ,,	9·78	22 ,,	9·48	0·00011
32 ,,	9·75	31 ,,	9·31	0·00012
48½ ,,	9·74	47½ ,,	9·05	0·00012
55 ,,	9·71	54 ,,	8·97	0·00012
72 ,,	9·67	71 ,,	8·76	0·00012
79 ,,	9·64	78 ,,	8·65	0·00013
95 ,,	9·60	94 ,,	8·51	0·00012
152 ,,	9·58	151 ,,	8·16	0·00011
168 ,,	9·57	167 ,,	8·03	0·00011
*48 days	7·82	*48 days	†7·12	
49 ,,	7·72			$k = 0·00011$
50 ,,	7·64			
51 ,,	7·56		Half-change period = 95 hours (obs.).	

* Sample taken from a silica flask which had been kept in the thermostat at 20° during the whole of the preceding period.

† Slight rise in the next 2 days.

A " period of induction," such as that recorded above, is conclusive evidence of the existence of *a preliminary phase preceding and holding up the main action.* In the case of a mutarotation this phase may be either (i) the first of a series of successive chemical changes, differing from the subsequent stages only in that it does not produce any marked alteration of rotatory power (compare the mutarotation of camphorcarboxylamide and camphorcarboxypiperidide, J., 1913, **103**, 913), or (ii) a period of time during which a pure material is taking up the impurities that are needed to promote the change, or an impure material is getting rid of some foreign substance which inhibits it. These two alternatives can be distinguished by the regularity and constancy of the period of

induction in the first case, and by its irregularity in the second. Since Baker, Ingold, and Thorpe (*loc. cit.*) did not record any period of induction in the mutarotation of tetra-acetylglucose in ethyl acetate, and since we did not observe any period of induction in ethyl acetate to which water had been added, there can be no doubt that the period of induction now recorded was of the latter type. In particular, it appears probable that, when a period of induction was observed, we were fortunate enough to be working with a system from which some ingredient, essential for the promotion of the chemical change, was initially absent but gradually appeared in the solution during the course of the first 20 hours, whilst in the experiments in which no period of induction was recorded this essential catalyst was already present when the solution was first examined.

(*b*) *Experiments with " wet " ethyl acetate.* The acceleration, shown in Table II (*b*), which was produced by adding 2·4% of water to the " dry " ethyl acetate was very marked. If compared with the complete arrest of mutarotation during the first 10 hours in " dry " ethyl acetate, the ratio of the velocities is, of course, infinite; but even when the average velocity during the first week is taken as a standard of comparison, the change in the " wet " ethyl acetate was ten times as fast as in the dry solvent. If, however, we compare the acceleration produced by adding water to ethyl acetate with the normal velocity of mutarotation in water itself, we find that the activity of the water in ethyl acetate corresponds to an active mass which is less than half of its total concentration.

(*c*) *Comparison with previous observations.* If the data recorded above for the velocities of mutarotation in dry and wet ethyl acetate were plotted on a velocity–concentration diagram, they could only be joined by a diagonal line passing through the origin, of the same general character as the line * labelled " Theoretical for Lowry or Armstrong's Mechanism " in the diagram in which Baker, Ingold, and Thorpe (J., 1924, **125**, 281) plot their own experimental results as four points on a horizontal straight line labelled " Theoretical for Jacobson and Stelzner's

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* This straight line is a graphical expression of the fallacy of identifying the activity of the water with its total concentration, rather than an expression of the essential requirements of a hydrate theory of catalysis. The responsibility for this line obviously belongs to the authors who drew it, and not to Lowry or Armstrong, whose names have been attached to it. In the same way, it would be unreasonable to hold Jacobson and Stelzner responsible for the horizontal line which expresses the fallacy that the velocity of isomeric change is independent of the concentration of the catalyst by which the change is determined.

Mechanism." It has already been suggested under (a) above that the failure of their line to pass through the origin was due to the use of incompletely purified materials; it is now necessary to inquire why our experiments show an increased velocity of muta-rotation in presence of added water, whilst their data showed no such acceleration. The answer to this question is very simple, since it can be calculated that, even if the catalytic activity of the water were proportional to its total concentration, the acceler-ation produced by 1% of added water would increase the velocity coefficient at 20° by about 0·0001 only, i.e., it would give rise to a velocity of the same order of magnitude as the lowest value recorded for mutarotation in dry benzene. The data in Table II show that in presence of a large excess of ethyl acetate the effect is even less than this, since 2·4% of water was required to give a velocity coefficient of the order of 0·0001. Since the half-change period for 2·4% of water is 95 hours, the " calculated " half-change periods for the concentrations of added water used by Baker, Ingold, and Thorpe would be 95 days for 0·1% of water and about a year for 0·025% of water. It has, moreover, been shown already that water in the presence of ethyl acetate is less efficient in pro-moting mutarotation than is water in the absence of ethyl acetate, obviously because the sugar has to compete with the solvent for possession of the catalyst. This effect is likely to be exaggerated when the concentration of the water is reduced, so that the excess of ethyl acetate is still larger; the effect of adding minute quantities of water would then be of a second order of minuteness, and could be detected only with the help of much more refined methods of examination than those which have been used hitherto.

6. *Experiments with Methyl and Ethyl Alcohols.*

(a) *Methyl alcohol.* Three new series of experiments on the velocity of mutarotation of glucose and of tetramethylglucose in dried methyl alcohol of known water content (purified by the method of Regnault as improved by Jones, McCombie, and Scarborough, J., 1923, **123**, 2694, and finally distilled from quicklime) are set out in Table III.

If we assume that the velocity of mutarotation would be increased about five-fold by the rise of temperature from 20° to 44·8°, the value recorded by Baker, Ingold, and Thorpe for glucose in " dry " methyl alcohol would (on reduction to the lower temperature and conversion to minutes as the unit of time) be about 0·0005 at 20° and would therefore be of the same order of magnitude as the values 0·0008, 0·0006, and 0·0004 which we have observed for glucose and for tetramethylglucose in methyl alcohol containing

TABLE III.

Mutarotation of Glucose and of Tetramethylglucose in Methyl Alcohol.

(In 6-dcm. glass polarimeter tubes at 20°.)

Glucose in dried methyl alcohol (99·8%) (shaken together and filtered).			Glucose in dried methyl alcohol (99·5%) (shaken together and filtered).			Tetramethylglucose in dried methyl alcohol (99·5%) (10 g./100 c.c.).		
Time.	a_{5461}.	$k \times 10^3$.	Time.	a_{5461}.	$k \times 10^3$.	Time.	a_{5461}.	$k \times 10^3$.
45 min.	6·32	—	10 min.	8·24	—	1 hour	72·82	—
1 hour	6·28	—	25 ,,	8·21	0·63	2 hours	72·52	0·39
2 hours	6·19	0·71	1 hour	8·15	0·62	4 ,,	71·92	0·40
3 ,,	6·06	0·83	2 hours	8·04	0·62	6 ,,	71·34	0·40
4 ,,	5·92	[0·90]	3 ,,	7·95	0·59	9½ ,,	70·44	0·39
5 ,,	5·85	0·82	4 ,,	7·86	0·59	22½ ,,	67·65	0·39
6 ,,	5·74	0·84	6 ,,	7·68	0·59	30½ ,,	66·46	0·38
9½ ,,	5·44	0·83	22 ,,	6·62	0·59	46½ ,,	64·36	0·38
22 ,,	4·70	0·82	31 ,,	6·25	0·59	55½ ,,	63·57	0·38
26½ ,,	4·52	0·83	47 ,,	5·81	0·59	71 ,,	62·40	0·38
30 ,,	4·42	0·82	56 ,,	5·64	0·56	82½ ,,	61·24	0·45
46 ,,	4·09	0·83				95 ,,	61·23	0·39
49 ,,	4·06	0·81	Final	5·24		102¾ ,,	60·93	0·39
70 ,,	3·96	0·70				10 days	59·76	
74 ,,	3·92	[0·60]						
78 ,,	3·90	0·75						
96 ,,	3·82							
100 ,,	3·84							

$k = 0.00080$	$k = 0.00060$	$k = 0.00039$
Half-change period = 15 hours.	Half-change period = 20 hours.	Half-change period = 30 hours.

rather more than 99½% MeOH. Our values for glucose at 20°, however, show an erratic behaviour that cannot be seen in the data for 44·8° (where only a single sample of alcohol and of sugar was examined), since the sample of methyl alcohol which had the larger water content had the smaller catalytic activity. Moreover, tetramethylglucose, which gives nearly the same velocity co-efficients as glucose in water (and happens to give an identical velocity in aqueous methyl alcohol containing 20% of water), was now seen to change much more slowly than glucose, a result that must, we think, be attributed to the greater purity of the tetra-methylglucose.

The fact that a finite velocity was observed for a solution in methyl alcohol of the same sample of tetramethylglucose which had exhibited an arrest of mutarotation in ethyl acetate and in chloroform is sufficient to prove that this residual velocity cannot have been due to impurities in the sugar. Moreover, since each 1% of added water has been found to increase the velocity of mutarotation by only about 0·00008 in minute-units at 20°, it is clear that a velocity of 0·0004 would correspond with the presence of about 5% of water in a sample which was shown by deter-minations of density to contain less than 0·5% of water. The

residual velocity of mutarotation of tetramethylglucose in methyl alcohol cannot therefore have been due either (i) to impurities in the sugar, or (ii) to water in the alcohol, and must therefore be attributed either (iii) to the presence in the alcohol of some unknown catalyst, other than water, or (iv) to catalysis by the alcohol itself, apart from the direct catalytic action of the small amount of water which it contained. The latter alternative is perhaps the more reasonable, but the former alternative cannot yet be excluded. If the alcohol is not a catalyst, it may be possible to establish this fact by using some more effective method of purification in order to produce an arrest of mutarotation in this solvent. If the alcohol

FIG. 1.

FIG. 2.

Mutarotation of tetramethylglucose in " dry " and " wet " ethyl acetate.
× dry.   o wet.

Mutarotation of tetramethylglucose and glucose in " dry " pyridine.
o glucose.   × tetramethylglucose.
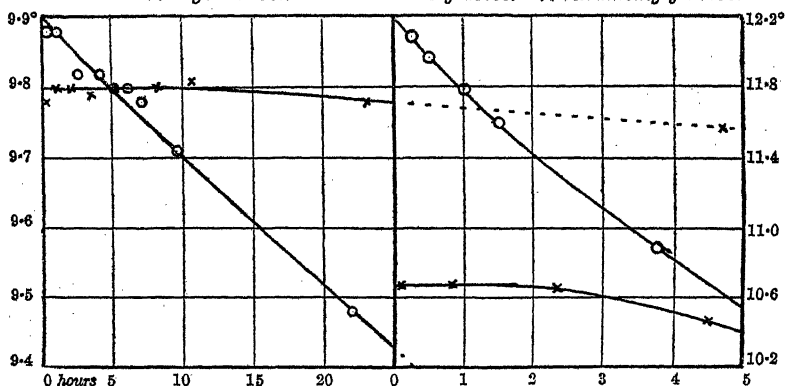
is a catalyst, this direct proof will not be possible, but it is hoped that an indirect method of attack may lead to a definite solution of the problem.

7. *Experiments with Pyridine* (Fig. 2).

(*a*) *Glucose.* Data showing the mutarotation of glucose, and of tetramethylglucose in anhydrous pyridine at 20° are set out in Table IV. The velocity of mutarotation of glucose in a mixture of 1 part of pyridine with about 6 parts of water has been found to be perhaps 18 times more than in water. On the other hand, the velocity in " dry " pyridine as shown in Table IV (*a*) and (*b*) is about 15 times *less* than in water. This velocity may perhaps be reduced by further purification, but we have already proved that, when due allowance is made for differences of concentration, pyridine in the presence of an excess of water is at least 2000 times more efficient as a catalyst than pyridine in the absence of water.

TABLE IV.

Mutarotation of Glucose and Tetramethylglucose in Anhydrous Pyridine at 20°.

(a) Glucose* (shaken and filtered).			(b) Glucose (shaken and filtered.) (Second sample of pyridine.)			(c) Tetramethylglucose (1 g. in 25 c.c.; filtered).	
Time (mins.).	a_{5461}.	$k \times 10^3$ (min.).	Time (mins.).	a_{5461}.	$k \times 10^3$ (min.).	Time (mins.).	a_{5461}.
15	12·09°	—	10	10·16°	—	5	10·67'
30	11·97	[1·34]	20	9·99	—	50	10·67
60	11·79	1·14	30	10·02	1·0	140	10·65
90	11·60	1·12	45	9·94	1·1	270	10·46
125	11·44	1·03	60	9·87	1·0	1280	8·43
225	10·88	1·06	90	9·73	1·1	1670	7·80
390	10·14	1·03	135	9·60	0·9		
1125	7·93	1·04	195	9·35	1·0		
1585	7·17	1·07	225	9·18	0·9		
Final	6·03		385	8·83	0·8		
(120 h.)			Final	5·35	—		

$$k = 0.00107 \qquad\qquad k = 0.0010$$

Half-change period = 9 hours.   Half-change period = 10 hours.

* The three readings of Behrend and Roth for the mutarotation of glucose in dried pyridine at 0° and with sodium light happen to fit almost perfectly on to this curve.

(b) *Tetramethylglucose.* In the case of tetramethylglucose, the rapid mutarotation shown in Table IV (c) was preceded by a " period of induction " (Fig. 2) during which mutarotation was arrested completely during a period of 2 hours. Mutarotation then began slowly, but proceeded with increasing speed, so that it was almost completed during the following night, but with the production of a green solution. The pyridine for this experiment had been dried with very great care, by a three-fold treatment with barium oxide, for use as a condensing agent in the preparation of co-ordination compounds; but it had not been purified in any other special way, and may have contained a mixture of bases, including the reactive α-derivatives of pyridine. Careful drying, therefore, stopped the action completely for a short time; but as soon as a sufficient supply of an auxiliary catalyst had been obtained the mutarotation was rapid, and proceeded to completion in a shorter period than in the corresponding experiment with glucose.

(c) Pyridine is a tertiary base of a particularly stable type, from which it would be impossible to remove a proton without the use of drastic chemical agents, such as are used in chlorination or nitration. We do not expect, therefore, to be able to repeat this observation with anhydrous ammonia which (like water) can either gain or lose a proton. The experiment might also be difficult

to repeat with a stronger base, since the velocity of mutarotation probably depends on the product (or some similar function) of the basic and acid dissociation constants of the medium, as well as of the sugar; a stronger base might therefore require only minute traces of water in order to develop a catalytic activity of sufficient intensity to produce an almost instantaneous mutarotation. This · conclusion has an important bearing on the experiment with tetramethylglucose which has just been described, since the results observed would obviously follow if the liquid contained bases which *when acting in presence of water* had a higher catalytic activity than that which is developed by pyridine under the same conditions.

8. *Summary.*

(a) Although glucose is unsuitable for use in experiments on the arrest of mutarotation, the *tetramethylglucose* of Purdie and Irvine is an ideal sugar for this purpose, on account of its ready solubility in anhydrous solvents, and of the possibility of adequate purification by crystallising it from such solvents. Its behaviour has therefore been studied in chloroform, benzene, ethyl acetate, methyl alcohol and pyridine.

(b) The mutarotation in *chloroform* was (in one instance only) arrested during a period of 10 days, just as was formerly observed in the case of nitrocamphor; this arrest is attributed to the elimination of catalysts by carbonyl chloride derived from the chloroform by oxidation.

(c) The velocity of mutarotation in *benzene* was reduced from 0·0008 to 0·0001 by careful drying, but a very rapid mutarotation was produced by the addition of water; this was attributed to the possible presence in the benzene of water-soluble impurities which developed strong catalytic properties only after association with water.

(d) The mutarotation in *ethyl acetate* was preceded by a period of induction extending over about a day; this solvent, therefore, appears to possess no catalytic properties of its own in the absence of an auxiliary catalyst. In presence of small quantities of water, mutarotation proceeded without a period of induction.

(e) No arrest or period of induction was observed in the mutarotation of glucose in *methyl alcohol* or of tetramethylglucose in *methyl* or *ethyl alcohol*. It is therefore possible that methyl alcohol is a real catalyst for the mutarotation of the sugars, although thirty times less efficient than water; but this view is based only on negative evidence, since it is possible that further purification may reduce (or even eliminate) the small residue of catalytic activity which it appears to possess.

(*f*) The velocity of mutarotation of glucose in *pyridine*, to which no water has been added, is very small, but no arrest of mutarotation has yet been recorded. The mutarotation of tetramethylglucose in pyridine, however, was preceded by a short period of induction; this shows that the change is not spontaneous, but depends on the presence of an auxiliary catalyst.

(*g*) A clear distinction is drawn between (i) *inactive solvents* such as chloroform, which have no catalytic properties; (ii) *ampholytic solvents* such as water, which can act as *complete catalysts*; (iii) solvents such as pyridine, which are not catalysts when pure, but develop catalytic properties in presence of an *auxiliary catalyst ;* the *mixed catalysts* formed in this way are more efficient than the *complete catalysts*, and often give rise to a mutarotation which is too fast to be followed experimentally.

CXC.—*The Constitution of Soap Solutions in Presence of Electrolytes. Potassium Laurate and Potassium Chloride.*

By WILLIAM CLIFFORD QUICK.

BY combining measurements of conductivity with those of osmotic activity (*e.g.*, freezing-point depression), the nature and amount of the various constituents of soap solutions have been deduced.[*] The addition of a salt necessitates the use of a third method. The determination of the transference of each of the constituents of the solution during electrolysis is perhaps the most decisive physicochemical method, when it is applicable, for it decides beyond question what are the constituents which conduct the current. In the present study, potassium laurate was chosen as a typical and stable soap, soluble at the ordinary temperature even in the presence of large amounts of potassium chloride. All three methods have been made use of and it has been shown that soap and salt mutually

* For references, see " The Study of Soap Solutions and its Bearing upon Colloid Chemistry." Union Internationale de la Chimie Pure et Appliquée, Cambridge, June, 1923; *J. Soc. Chem. Ind.*, 1923, **42**, 615; *Chim. et Ind.*, 1924, **11**, 3; *Amer. Dyestuff Rep.*, 1923, **12**, 822.

depress each other's dissociation; further, a value is deduced for the hydration of the colloid in solution which agrees with that previously determined by the method of ultrafiltration.

EXPERIMENTAL.

Materials.—The purest materials obtainable were used in all these experiments. In migration experiments 1 to 5 the potassium laurate used (from Kahlbaum) was 0·5% (equiv.) alkaline. The potassium sulphate and chloride employed were Kahlbaum's " zur Analyse." The 7% solutions of the latter are barely alkaline to phenolphthalein; which would very slightly affect the anode and cathode results in opposite directions. The potassium chloride was heated in a silica dish before the solutions were made up. In migration experiments 6 and 9 the potassium laurate was made from Kahlbaum's lauric acid (M 199·18) and pure potassium hydroxide (see Bunbury and Martin, J., 1914, **105**, 417). All the precautions described in previous communications were taken with standard solutions, solvents, vaselin, and apparatus.

Conductivity.—A complete series of conductivity measurements at 18° has been carried out with a solution containing 1 g.-mol. of potassium laurate in 1 kg. of water ($1·0N_w$) to which potassium chloride was added in quantities varying from 0·5 mol. to 3·5 mols. ($3·5N_w$). The cell was of the special high-resistance type described by McBain, Laing, and Titley (J., 1919, **115**, 1282).

Osmotic Activity.—The osmotic activity of the same series of mixtures as those used in the conductivity measurements has been determined by the method of dew-point lowering (McBain and Salmon, *J. Amer. Chem. Soc.*, 1920, **42**, 426). The lowering of freezing-point method is not applicable in the case of these mixtures, although it can be used with pure potassium laurate solutions up to 1·0 N_w, because addition of electrolyte greatly reduces the solubility of curd fibres (compare J., 1922, **121**, 1320).

Electrolytic Migration.—The migration apparatus was the same as that used by McBain and Bowden (J., 1923, **123**, 2417). Guard solutions of potassium sulphate (7%) were most satisfactory for solutions containing potassium laurate and potassium chloride (up to 1·0N_w with respect to each), being of the correct density to give a sharp boundary between guard solution and soap solution, but not of sufficient concentration to cause salting out. For the mixture 1·0N_w-potassium laurate and 2·5N_w-potassium chloride, even saturated solutions of potassium sulphate failed to give a clear boundary line. A solution containing 7% of potassium sulphate and 12% of sucrose was finally used. Sucrose, as Washburn has shown (*J. Amer. Chem. Soc.*, 1909, **31**, 322), has no tendency to

move with the current, and although any slight oxidation at the anode would have a corresponding effect on the potassium value, the experiment would be otherwise unaffected by its presence. All solutions were clear and homogeneous when measured, except for a slight cloudiness at the anode to be mentioned later.

To introduce the most viscous solution, namely, $2·5N_w$-potassium chloride and $1·0N_w$-potassium laurate, into the apparatus, a pipette closed at the bottom and having a fairly large hole in each side was used, in order to ensure a sharp boundary with the guard solution. Wide-mouthed pipettes were used for the removal of the solution from the apparatus. Even with these precautions the handling of the viscous liquid was so slow that the analytical data were considerably affected. The results, which are not given in the tables, show from analyses at the anode that the soap carries at the least 3—4% and at the most 10% of the total current. Analysis at the cathode gave a migration number of 0·48 for the chlorine, thus leaving a migration number of 0·02 or about 4% of the current for the soap. The soap solutions containing less salt were quite mobile.

The total current was measured by a silver coulometer on each side of the apparatus, any electrical leak thus being detectable. The best deposits of silver were obtained by using 10% solutions of silver nitrate with currents of 17 to 20 milliamps. Smaller currents tend to give loose deposits which are difficult to wash without loss of silver. With good deposits of silver, the coulometers agreed to 0·1%. By passing the current for about 2 hours, a deposit of about 0·16 g. of silver was obtained.

Analytical Methods.—After the passage of the current seven portions of the solution were analysed. In experiments 1 to 5 McBain and Bowden's method of soap analysis (*loc. cit.*) was used. The results thus obtained, however, were inaccurate, and in all later experiments the following method was used. A known quantity (excess) of $0·5N_v$-sulphuric acid was added to a weighed portion of the solution, the mixture was shaken with three successive quantities of about 25 c.c. of chloroform, the chloroform solution of lauric acid removed, and the excess of sulphuric acid in the aqueous layer titrated with $0·1N_v$-sodium hydroxide. The solution of lauric acid was boiled to expel carbon dioxide and, while still hot, titrated with $0·25N_v$-alcoholic sodium hydroxide and phenolphthalein; by the careful addition of water as the titration proceeded a good end-point was obtained in a clear homogeneous solution.

The chloride in the aqueous layer was then estimated gravimetrically as silver chloride. In the anode and cathode portions containing the potassium sulphate from the guard solutions special

care was taken to avoid the precipitation of silver sulphate. The solution was diluted to about 600 c.c. before precipitation, and a larger quantity than usual of nitric acid was added, and silver nitrate only in slight excess. A small sample of the "middle-middle" portion (MM) was reserved for qualitative testing for sulphate in each experiment. At least one sample of the original mixture was analysed in each migration experiment.

Calculation of Data.—All analytical data are expressed in weight normality (N_w). The weights of potassium laurate and potassium chloride were obtained from the analysis, and that of the water by difference. The equivalent change of each constituent produced by electrolysis was referred to the weight of the same constituent associated with an equal weight of water in the original mixture. In calculating the change in the concentration of potassium ion the total potassium must be considered, being the equivalent of the $N/2$-sulphuric acid used to split up the soap + potassium associated with chloride (= total equivalent of chloride by analysis).

The weights of oxygen and hydrogen evolved at the anode and the cathode, as calculated from the coulometer reading, are added to the weights. Each experiment gives four independent determinations of the migration number of potassium, but only two of laurate and chloride.

The total number of equivalents transported should be equal to the coulometer equivalents; *i.e.*, if the sign of the migration number of the anion or the kation is changed, then the migration of anion + kation should be equal to ± 1. For example, the algebraic sum of the quantities of potassium, laurate and chloride transported should equal unity. This fact provides a check on the accuracy of the data in each experiment where the data are complete.

Experimental Data.—The conductivity measurements are given in Table I. The values given as "molecular conductivity" (μ) are calculated with respect to normality of total potassium element.

Table II contains the results obtained from determinations of the lowering of dew point.

Table III gives the results of migration experiments using solutions of potassium laurate without added salt. The data for $1 \cdot 0 N_w$-solution confirm Bowden's result obtained at this concentration, and comparison of migration 6 with his data clearly shows the greater accuracy of the new method of analysis.

Table IV contains migration data for mixtures of $1 \cdot 0 N_w$-potassium laurate and $1 \cdot 0 N_w$-potassium chloride. The migration of chlorine takes a peculiar form, a large gain in the anode compartment being followed by a fairly large loss in the adjoining anode middle

TABLE I.

Conductivities at 18°.

Solutions $1\cdot0N_w$ with respect to potassium laurate.

KCl (N_w).	Spec. cond. $\kappa \times 10^{-2}$.	True density at 18°.	Mol. cond. μ.	KCl (N_w).	Spec. cond. $\kappa \times 10^{-2}$.	True density at 18°.	Mol. cond. μ
—	3·824			1·5	13·31	1·0665	67·41
	3·889		47·09		12·50		63·29
	3·886			2·0	15·40	1·0819	65·76
0·5	7·226	1·0346	59·35		15·38		65·68
	7·174		58·93	2·5	17·87	1·0972	66·27
0·7	8·289	1·0423	59·71	3·0	20·07	1·1126	65·90
1·0	10·064	1·0525	62·72		19·88		65·30
	10·090		62·87	3·5	21·97	1·1275	64·96

The value for $1\cdot0N_w$-potassium laurate without salt, given for comparison, is from McBain, Laing, and Titley (J., 1919, **115**, 1282).
Cell constant at the beginning of the series, 14·02; at the end, 14·05.

TABLE II.

Dew-point Lowering and Osmotic Activity at 18°.

Solutions $1\cdot0N_w$ with respect to potassium laurate.

KCl (N_w).	Dew-point lowering.	Mean.	KCl (N_w).	Dew-point lowering.	Mean.
0·5	0·45, 0·41, 0·44, 0·45	0·44	2·0	1·27, 1·30	1·28
0·7	0·57, 0·57	0·57	2·5	1·41, 1·43, 1·41	1·42
1·0	0·77, 0·78, 0·75, 0·77	0·77	3·0	1·69, 1·73	1·70
1·5	1·02, 0·96, 1·04	1·01	3·5	(1·88), 2·07, 1·97	1·9(7)

Apparent concentration of crystalloid = dew-point lowering/0·30.

TABLE III.

Migration Data for $1\cdot0N_w$-Potassium Laurate (without added salt).

Expt. 2. Temp. 18°. Analysis of original solution : K = $0\cdot970N_w$, L = $0\cdot963N_w$. Current of 22 milliamps. passed for 105 mins. Coulometer equiv. = 0·001241 equiv. of silver.

Portion.	Equivalents change.		Transference number (n).		
	K.	L.	K analysis.	L analysis.	Mean.
Anode	−0·459	+0·634			
AM	+0·030	+0·094	0·55	0·81	
AMM	−0·018	+0·083			
MM	+0·059	+0·168			$n = 0\cdot53$
CMM	−0·041	+0·048			
CM	+0·028	+0·049	0·46	0·31	
Cathode	+0·557	−0·402			

Expt. 3. Temp. 14·5°. Analysis of original solution : K = $1\cdot002N_w$, L = $1\cdot001N_w$. Current of 20 milliamps. passed for 135 mins. Coulometer equiv. = 0·001697 equiv. of silver.

Portion.	K.	L.	K analysis.	L analysis.	Mean.
Anode	−0·434	+0·540			
AM	−0·037	−0·016	0·54	0·54	
AMM	+0·006	+0·014			
MM	−0·008	−0·007			$n = 0\cdot51$
CMM	−0·005	−0·007			
CM	±0·000	±0·000	0·47	0·50	
Cathode	+0·533	−0·494			

TABLE IV.

Migration Data for 1·0N$_w$-Potassium Laurate + 1·0N$_w$-Potassium Chloride.

Expt. 6. Temp. 14°. Analysis of original mixture : Soap, K = 0·984N$_w$, L = 0·969N$_w$; KCl = 0·995N$_w$; total K = 1·979N$_w$. Current of 21 milliamps. passed for 120 mins. Coulometer equiv. = 0·01591 equiv. of silver.

Portion.	Equivalents change.			Transference numbers.			Mean values.
	K.	L.	Cl.	K.	L.	Cl.	
Anode ⎫	*	+0·283	—				
AM ⎬	—0·61	—0·094	—	(0·61)	0·21	—	L = 0·23
AMM ⎭		+0·025	—				
MM	—0·03	—0·010	±0·00				Cl = 0·31
CMM	—0·01	—0·023	+0·007				(L + Cl) as
CM	—0·06	—0·023	—0·005	0·41	0·26	0·31	K = 0·46
Cathode	+0·46	—0·217	—0·314				K = 0·49

* This value for K is obtained if Cl = 0·30.

Expt. 4. Temp. 15·5°. Analysis of original mixture : Soap, K = 0·991N$_w$, L = 0·974N$_w$; KCl = 0·997N$_w$; total K = 1·988N$_w$. Current of 19·5 milliamps. passed for 130 mins. Coulometer equiv. = 0·001543 equiv. of silver.

Anode	—0·44	+0·494	+1·058				
AM	—	—0·299	—	—	+0·14	—	L = 0·17
AMM	+0·016	—0·049	—0·132				
MM	—0·04	—0·021	—0·026				Cl = 0·26
CMM	±0·00	+0·006	—0·032				(L + Cl) as
CM	—0·134	—0·072	—0·161	(0·70)	0·20	0·26	K = 0·54
Cathode	+0·836	—0·132	—0·036				

Expt. 5. Temp. 15°. Analysis of original mixture : Soap, K = 0·991N$_w$, L = 0·974N$_w$; KCl = 0·997N$_w$; total K = 1·988N$_w$. Current of 20 milliamps. passed for 165 mins. Coulometer equiv. = 0·00194 equiv. of silver.

Anode	+0·646	+0·522	+1·072				
AM	—0·736	—0·210	—0·516	(0·26)	0·25	0·43	(L + Cl) as
AMM	—0·124	—0·046	—0·089				K = 0·52
MM	—0·040	—0·018	—0·030				L = 0·18
CMM	—0·014	±0·000	—0·012				
CM	—0·143	—0·004	—0·161	(0·77)	0·12		
Cathode	+0·913	—0·118	±0·000				

Expt. 7. Temp. 13°. Analysis of original mixture : Soap, K = 1·001N$_w$, L = 0·997N$_w$; KCl = 1·005N$_w$; total K = 2·006N$_w$. Current of 21 milliamps. passed for 120 mins. Coulometer equiv. = 0·001567 equiv. of silver.

Anode	+0·470	+0·516	+0·950				
AM	—0·742	—0·218	—0·517	—0·48	+0·24	+0·31	(L + Cl) as
AMM	—0·207	—0·055	—0·126				K = 0·51
MM	—0·054	—0·003	—0·051				
CMM	—0·051	+0·002	—0·032				K = 0·50
CM	—0·193	—0·012	—0·157	+0·51	—0·14	—0·29	L = 0·19
Cathode	+0·756	—0·129	—0·097				Cl = 0·30

Final values for migration numbers in 1·0N$_w$-K Laurate + $\left\{ \begin{array}{l} \text{K} = 0·47 \\ \text{L} = 0·19 \\ \text{Cl} = 0·32 \end{array} \right.$
      1·0N$_w$-KCl ....
                    i.e., K + L + Cl = 0·98.

(AM) portion; whilst at the cathode there is scarcely any loss. A similar effect is seen in the apparent movement of the fatty acid and potassium. This phenomenon cannot be due to mixing,

as the boundaries remain undisturbed throughout; it may be explained, however, when we remember that the soap mixture is more than twice as concentrated as the guard solution and therefore tends to imbibe water.

Discussion.

McBain and his collaborators have shown that under given conditions the constituents of a soap solution, viz., neutral colloid, ionic micelle, and simple crystalloid, are in true, reversible equilibrium. The work of McBain and Burnett (J., 1922, **121**, 1320) has also established the fact that the equilibrium colloid $\rightleftharpoons$ crystalloid in any particular solution under given conditions is remarkably definite in presence of added electrolyte. It may therefore be expected that any or all of the above-mentioned constituents of a pure soap solution will be affected in a definite and reproducible manner by the addition of a salt. We must consider the possibility of change not only in the proportions of micelle and neutral colloid but also in their nature.

Trustworthy information on the subject of transport numbers is essential for any solution of the problem. The fraction of the total conductivity of the solution due to any one constituent is dependent on its concentration and mobility and equally on the total conductivity of the solution. Therefore the total conductivity must be resolved as the sum of the conductivities of all the various conducting constituents according to an expression (Laing, J. Physical Chem., 1924, **28**, 673) of the form

$$n = (cv + c_1 m_1 f_1 + c_2 m_2 f_2)/\mu,$$

where m = number of chemical equivalents of a particular constituent which carry one electric charge, f = conductivity in mhos of one chemical equivalent of the same constituent (v for Cl', f_1 for ionic micelle, f_2 for neutral colloid), n = migration number, μ = conductivity in mhos of that amount of solution containing 1000 g. of water and c equivalents of the constituent, and c = number of chemical equivalents of the constituent per 1000 g. of water.

The value obtained for the transport of total potassium in these mixtures, 0·47, allows us to conclude that there can be very little movement of neutral colloid. If $m_2 f_2$, the effective mobility of the neutral colloid, had been as great in pure soap solution, viz., 20 mhos, its apparent migration towards the anode, $n_2 = c_2 m_2 f_2/\mu$, would have been 0·10 in $1 \cdot 0 N_w$-potassium laurate $+ 1 \cdot 0 N_w$-potassium chloride. But the total movement of potassium, 0·47, towards the cathode differs by 0·03 unit from the value, 0·50, that would be given either by potassium chloride or by potassium ion $+$ ionic micelle alone. Hence the effective mobility of the neutral colloid

3 B*

is $20 \times 0.03/0.10 = 6$ mhos. Mukherjee and Roy (J., 1924, **125**, 476) have pointed out that the effect of the addition of an electrolyte with univalent ions to a charged colloid is gradually to neutralise the charge by electrical adsorption of ions of opposite sign to that of the charged colloid, reversal of sign being impossible. Thus we might expect the " neutral colloid," which is only very slightly charged in pure soap solutions, to move still less in these mixtures.*

A second main conclusion to be drawn with certainty from the migration data for $1.0N_w$-potassium laurate $+ 1.0N_w$-potassium chloride is that the soap conducts nearly two-fifths of the current. This corresponds to the conducting power of the soap in $1.0N_w$-potassium laurate alone. If we assume that the mobility of the ionic micelle in the mixture is approximately the same as in $1.0N_w$-potassium laurate alone, the mobilities of K·, Cl′ and $(L')_n$ are identical. From Table V the concentration of K· is 0.97 and that of $(L')_n + $ Cl′ is necessarily equivalent to it, making a total concentration of conducting constituents of $1.94N_w$. Hence the concentration of $(L')_n = 1.94 \times 0.19 = 0.37N_w$, and the concentration of Cl′ $= 1.94 \times 0.31 = 0.60N_w$. Thus, unless we are to assume that the mobility of the ionic micelle is very greatly enhanced, its concentration cannot be greatly decreased by this concentration of added electrolyte. We should, however, expect some increase in the mobility of the micelle, which leads to the conclusion that its concentration must be less than in $1.0N_w$-potassium laurate alone and that the concentration of the chlorine ion is rather higher than $0.60N_w$. In the absence of soap the concentration of chlorine ion in $1.0N_w$-potassium chloride as indicated by osmotic methods is $0.74N_w$.

In the case of the mixture $1.0N_w$-potassium laurate and $2.5N_w$-potassium chloride the soap still conducts a fraction of the current, but so small as to indicate that dissociation into ionic micelle has been diminished by the higher concentration of chloride. The experimental error in migration 9 allows us to place the migration of soap in $1.0N_w$-potassium laurate $+ 2.5N_w$-potassium chloride not higher than a maximum of 10%, which gives the concentration of ionic micelle as $0.18N_w$, assuming its mobility the same as K· and Cl′. As will be seen later, however, we have in the present case evidence that the hydration of the soap is decreased by the added electrolyte (compare McBain and Taylor, J., 1919, **115**, 1300; 1921, **119**, 1369; Bennett, J., 1924, **125**, 1971, etc., where added electrolyte causes dehydration of curd fibres of palmitate). In this case we should expect a micelle of greater mobility and thus

* A further detailed study will be published by Dr. M. E. Laing.

we may conclude that one effect of the added salt is the repression of the dissociation of the colloidal electrolyte.

The Hydration of the Soap.—The data also afford definite indications of the degree of hydration of the soap in solution. In previous communications from this laboratory it has been shown that the anion of the soap is an aggregate of fatty acid ions retaining their full electric charge and carrying water of hydration. In all except very dilute solutions the remainder of the soap is almost entirely in the form of neutral colloid. We may write : Neutral colloid = (K Laurate)$_x$,yH$_2$O and ionic micelle = (L')$_n$,mH$_2$O. In pure soap solutions also the ionic micelle has a mobility at least equal to that of the potassium ion or chlorine ion (64). Evidently the mobility will be influenced by changes in the degree of hydration. If we assume that the mobility of the ionic micelle is the same as in pure soap solutions, the mobilities of the potassium ion, the chlorine ion, and (L')$_n$ are each 65 mhos, which gives $u + v = \mu_\infty$ = 130. The concentration of K˙ is μ_v/μ times N_w of the total potassium in the solution. The total crystalloid in these mixtures is total potassium ion plus chlorine ion plus undissociated potassium chloride, *i.e.*, the concentration of the total crystalloid is (Normality of total chlorine plus potassium ion) or total chloride plus $\mu_v/\mu_\infty \times N_w$ of the total potassium in the solution. Now the osmotic activity gives the apparent concentration of crystalloid, but this value is enhanced because a portion of the solvent water is removed by hydration of the soap. Therefore we can calculate the hydration by means of the difference between *the concentration of total crystalloid* deduced from conductivity data and *the apparent concentration of crystalloid* obtained from the dew-point lowering. Take, for instance, the data for the solution 1·0N_w-potassium laurate and 1·0N_u-potassium chloride : $\mu_v/\mu_\infty = 62\cdot79/130$. Therefore [K˙] = 0·97$N_w$ and [total crystalloid] = 1·97N_w. The concentration of total crystalloid deduced from the lowering of dew-point is 2·57N_w. Therefore hydration = 23% of the total water (55 mols.) = 12·8 mols. of water per equivalent of soap.

Now, these values are not greatly affected by any possible deviations of the mobility of the ionic micelle from its assumed value, on account of decreased hydration. From the migration data we see that only 18% of the value of μ_∞ is due to the ionic micelle. Thus even an increase in the mobility of the micelle of one-fifth would only make $\mu_\infty = 135$; whence the mobility of K˙ = 0·93 and the hydration = 13·7, instead of 0·97 and 12·8, respectively.

In higher concentrations of potassium chloride the values of the concentration of K˙ and of the hydration of the soap are even less

dependent on the mobility of the ionic micelle, as a still smaller fraction of the total conductivity is due to the ionic micelle. In Table V, therefore, are given the values of the concentration of $K^{.}$ and of the hydration corresponding to a mobility of ionic micelle = 65 (= $K^{.}$ = Cl'). We may regard these values as being correct to within 1 mol. of H_2O and $\pm 0.02N_w$-$K^{.}$. This value, 12·8 mols. per equivalent, for the hydration of the soap in the solution $1.0N_w$-potassium laurate + $1.0N_w$-potassium chloride is in good agreement with the value, > 11·8, obtained by McBain and Jenkins (J., 1922, **121**, 2325) by the method of ultrafiltration. The experimental error in the case of the solution $0.5N_w$-potassium chloride + $1.0N_w$-potassium laurate is larger than that for a solution of higher concentration, a difference of $\pm 0.01°$ in the dew-point lowering corresponding with a difference of ± 1.1 mols. of water in the hydration value.

TABLE V.

Concentration (N_w) of the Constituents and the Total Hydration of the Soap in Solutions of $1.0N_w$-Potassium Laurate containing added Potassium Chloride at 18°.

KCl.	$K^{.}$	Total crystalloid.	Hydration. Mols. H_2O : 1 mol. KL.	KCl.	$K^{.}$	Total crystalloid.	Hydration. Mols. H_2O : 1 mol. KL.
0·5	0·68	1·18	11 (± 1.1)	2·0	1·52	3·52	9·6
0·7	0·78	1·48	12·2	2·5	1·78	4·28	5·2
1·0	0·97	1·97	12·8	3·0	2·02	5·02	6·3
1·5	1·26	2·76	10	3·5	2·25	5·75	6·9

No stress can be laid on the apparent minimum in the presence of $2.5N_w$-potassium chloride, although at this same concentration the conductivity and possibly also the viscosity has a maximum value.

The values in Table V for the concentrations of the potassium ion in the solutions $1.0N_w$-potassium laurate + $0.5N_w$-potassium chloride and $1.0N_w$-potassium laurate + $1.0N_w$-potassium chloride do not agree with the respective values of $0.38N_w$ and $0.79N_w$ obtained by Salmon from $E.M.F.$ measurements (J., 1922, **121**, 711). Also his value of $0.09N_w$ for the ionic micelle in the solution $1.0N_w$-potassium laurate + $1.0N_w$-potassium chloride appears to be much too low in view of the migration values obtained for this solution. Presumably the correction assumed by Salmon for diffusion potential is inadequate.

The value of $Cl' = 0.60N_w$ obtained from the transport of chloride in $1.0N_w$-potassium laurate + $1.0N_w$-potassium chloride and the molecular conductivity of the same solution indicates that the soap likewise diminishes the dissociation of the potassium chloride.

Summary.

Accurate determinations have been made of the transport of each of the constituents of a solution containing potassium laurate and potassium chloride during electrolysis.

In a solution which is weight normal with regard to both salt and soap, the quantities of potassium, laurate and chloride ions transported are 0·47, 0·19, and 0·32 equivalent, respectively.

Apparently, therefore, the undissociated soap (neutral colloid) scarcely moves in this solution, and the ionic micelle does not contain appreciable quantities of undissociated soap. This confirms previous work showing that the ionic micelle is a hydrated colloidal aggregate of simple fatty ions.

Since the migration of the potassium ion, 0·47, is nearly the same as in solutions of pure potassium chloride, whereas the migration number of the chlorine ion is only 0·32, only three-fifths of the total current is carried by potassium chloride, the remaining two-fifths being carried by ionised soap (ionic micelle).*

Salt and soap therefore mutually diminish each other's dissociation. Even when 2·5 equivalents of salt are added to a weight normal solution of laurate, there is still an appreciable quantity of dissociated soap (ionic micelle).

These data in conjunction with measurements of conductivity and of dew-point lowering enable us to evaluate the constituents present in these mixed solutions. Further, they show that the hydration of potassium laurate in $1·0N_w$-solution, where it is entirely colloidal (neutral colloid and ionic micelle), amounts to 12·8 mols. of water per equivalent of laurate. This confirms the value found by McBain and Jenkins by the wholly independent method of ultrafiltration.

An improvement in the method of analysis of solutions of soap is described in which filtration is replaced by extraction.

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* The mobilities of chlorine ion and ionic micelle are comparable with each other.

CXCI.—*Plant Cuticles.   Part I.   Modern Plant Cuticles. Studies in the Composition of Coal.*

By VERNON HOWES LEGG and RICHARD VERNON WHEELER.

A SERIES of researches on plant cuticles has been undertaken with a view ultimately to determine the constitution of cuticle as it occurs in bituminous coals, in conformity with the scheme of research outlined by Stopes and Wheeler (Monograph on the Constitution of Coal, London, 1918, p. 26).

The term cuticle was first used by Brongniart (*Ann. Sci. Nat.*, 1830, **21**, 427) to denote the outer protective covering which is common to all parts of plants.   Although from a botanical point of view the cuticle is a well-defined and easily recognisable constituent of the plant, yet its chemical nature has remained obscure.   The only chemical research on modern plant cuticle recorded in the literature appears to have been carried out by Frémy (*Compt. rend.*, 1859, **48**, 667 ; 1881, **92**, 926 ; 1885, **100**, 19) on the cuticle from ivy, apple and agave.   By means of boiling alkalis, Frémy resolved the cuticle from agave, after extraction with solvents, into two acids which were isolated in the form of their corresponding salts :   a solid acid which he termed stearocutic acid (C, 75·0 ; H, 10·7 ;   O, 14·3%), characterised by the insolubility of its potassium salt in water ; and a semi-liquid acid, oleocutic acid (C, 66·7 ;   H, 7·9 ;   O, 25·4%).   Frémy concluded that the characteristic constituent of cuticle, termed by him cutin or cutose, consists of a mixture of these two acids in the proportion of one part of stearocutic to five parts of oleocutic acid.   He observed (*Ann. Sci. Nat.*, 1882, **8**, 360) that similar products were obtained from purified cork, from which he concluded that suberin, the characteristic constituent of cork, is an impure form of cutose.   No evidence was adduced in support of this suggestion.   Similar views have been advanced by Mitscherlich (*Annalen*, 1850, **75**, 305), von Höhnel (*Bot. Z.*, 1878, **3**, 81) and by van Wisselingh (*Arch. Néerland.*, 1886, **20**, 95 ; 1888, **22**, 253 ; 1892, **26**, 305 ; 1895, **29**, 373), chiefly as a result of microchemical observations.   Since it will be shown in the present paper that the compounds which can be isolated from modern plant cuticle are indeed closely related both in properties and in composition to those obtained from cork, a brief reference should be made to the chemistry of the latter material.

By the action of alcoholic potash on purified cork, Kügler (Ueber das Suberin, Strassburg, 1884 ; *Arch. Pharm.*, 1884, **22**, 217) isolated stearic acid together with a crystalline acid known as

phellonic acid ($C_{22}H_{42}O_3$: C, 74·6; H, 11·7%), which, like stearo-cutic acid, forms a potassium salt insoluble in water. On the other hand, Gilson (*La Cellule*, 1890, **6**, 63), using the same reagent, isolated phellonic acid; a semi-liquid acid called suberinic acid, $C_{17}H_{30}O_3$; and a solid acid, phloïonic acid, for which he suggested the formula $C_{11}H_{21}O_4$ (an impossible one, assuming normal valencies). Schmidt (*Monatsh.*, 1904, **25**, 227, 302; 1910, **31**, 347) confined his attention more particularly to phellonic acid and in his first paper suggested the probable structure of this acid.

Some confusion has arisen from the use of the terms adipocellulose and cutocellulose by Cross and Bevan ("Cellulose," London, 1916, p. 225) and Cross and Dorée ("Researches on Cellulose, 1910—1921"; London, 1922, p. 188) for cork and cuticle respectively. In the latter, at all events, the outer layer of cuticle (as distinct from the cutinised layer) does not contain cellulose and the term cutocellulose is a misnomer. This point has been dealt with by Priestley (*The New Phytologist*, 1921, **20**, 17).

For the purpose of the present research, the cuticle from the *Agave americana* was chosen (as representing a typical modern plant cuticle) because the agave, in common with other tropical and sub-tropical plants, has a comparatively thick cuticle. The *Agave americana*, the most familiar species of agave, is a native of tropical America and is more familiarly known in this country as the century plant or American aloe. The plant consists of a large rosette of thick fleshy leaves around a central stem. It flowers only once in a number of years.

The crude cuticle, apart from about 4% of inorganic material, consisted only of carbon, hydrogen, and oxygen. A series of analyses on the material from different sources showed variations in composition between C 58·5 to 64·5 and H 8·8 to 9·3%, according to the age of the leaves, the cuticle from the most mature leaves containing most carbon and hydrogen.

By extraction with solvents it was found possible to resolve the crude material into four distinct classes of compounds, differing widely in properties and compositions : (1) Water-soluble material, 10%, containing about 48% of carbon; (2) wax, 15%, soluble in alcohol, benzene, and chloroform, containing about 79% of carbon; (3) cellulose, 14%, soluble in cuprammonia solution; and (4) a residue, 60%, insoluble in all the foregoing solvents and giving on analysis a consistent value for carbon of about 68%. This purified residue may be regarded as the characteristic constituent of cuticle and can be conveniently referred to by the term *cutin*. Our study has been chiefly of this residue. Three methods of attack have been employed : (1) Treatment with alcoholic potash; (2) destructive

distillation for the examination of liquid and gaseous products; and (3) oxidation.

After a comparatively short treatment with alcoholic potash, more than 90% of the cutin was resolved. Preliminary experiments showed that the alcoholic solution consisted almost entirely of a mixture of the potassium salts of different acids. Neither glycerol nor any other alcohol could be detected. A separation of the acid products was first effected by the somewhat complicated process employed by Gilson (*loc. cit.*), but a shorter method was subsequently worked out, based on the varying solubilities of the potassium salts in water, whereby almost identical products were isolated.

The chief product resulting from the action of alcoholic potash on cutin consists of a mixture of two semi-liquid acids which form potassium salts soluble in cold water. The greater portion of this mixture consists of an acid which forms a copper salt soluble in alcohol, whereas the copper salt of the remaining acid is insoluble in alcohol, so that a separation of the mixture into its constituent acids could be effected in this manner. Both acids (which are similar in composition) have a lower carbon content than the suberinic acid isolated by Gilson from cork, but in other respects their properties agree with those described for that acid. The analytical data, given in the experimental part of this paper, are in agreement with the formula $C_{26}H_{50}O_6$ for the acid obtained from the copper salt soluble in alcohol, and with the formula $C_{13}H_{22}O_3$ for the acid from the copper salt insoluble in alcohol. So far as we know, the occurrence of these acids in nature has not hitherto been recorded. We suggest that the names *cutic acid* for the former, which occurs in the greater quantity, and *cutinic acid* for the latter, would be appropriate.

In addition, two other acids have been isolated from the cutin, though in much smaller quantities, in the form of their sparingly soluble and insoluble potassium salts. From the sparingly soluble potassium salt the corresponding acid was obtained as a white, crystalline material which appears to be identical in composition and properties with the phloïonic acid isolated by Gilson from cork, but for which the formula $C_{19}H_{38}O_6$ appears to be more likely. From the insoluble potassium salt a still smaller quantity of a solid acid was obtained which has a somewhat higher carbon content than the phellonic acid isolated by Kügler and others from cork, but which appears to be closely related to that acid.

From the general description given by Frémy of his oleocutic and stearocutic acids, obtained from cuticle, it would appear that the former was a mixture of the two semi-liquid acids which we

Fig. 1.

Fig 2.

(a)

(c)

(b)
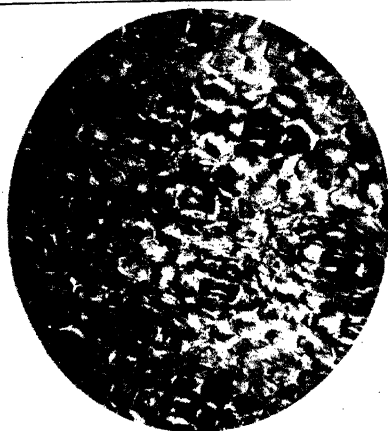
Surface view of raw cuticle from *Agave americana* showing impression of cells and stomata. (× .00).

Section of raw cuticle from *Agave americana* showing :—
(a) Outer layer of cuticle and "teeth,"
(b) Dark cutinised patches,
(c) Cellulose membrane (×100).

Fig. 3.

Fig. 4.

(a)

(b)

Surface view of purified cuticle from *Agave americana* showing structure persisting after treatment. (×100).
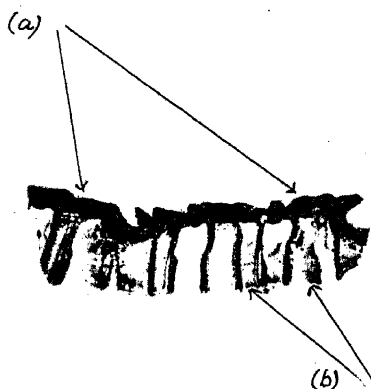
Section of purified cuticle from *Agave americana* showing :—
(a) Outer layer and " teeth " of *cutin*,
(b) Cutinised patches.
The cellulose membrane has been completely removed. (×100).

suggest should be termed cutic and cutinic acid respectively, and the latter was a mixture of phloïonic and phellonic acids.

A discussion of the results obtained on destructive distillation, and on oxidation, of cutin is reserved for a future communication, but it may be stated that on regulated distillation in a vacuum cutin yields a high proportion (60%) of tarry products, from which a hydrocarbon corresponding to pentatriacontane ($C_{35}H_{72}$) has been isolated.

<div align="center">E X P E R I M E N T A L.</div>

The first supplies of cuticle were obtained from some leaves of the *Agave americana* from the Botanical Gardens, Kew. The leaves were washed with water and the outer layer of cuticle peeled off as a continuous sheet. The amount of material thus obtained was small and only served for the preliminary experiments. Subsequently, some 2000 g. of cuticle, representing the supply from 50 large leaves, were obtained from the Division of Botany, Department of Agriculture, South Africa, and it was with this material that the majority of the work was carried out.

When dry, the cuticle forms a brittle tissue, light yellow in colour, but when moistened with water it readily becomes pliable. Photomicrographs illustrating the crude material, in surface view and section, are given in Figs. 1 and 2. From the surface view it will be seen that the cuticle retains the impress of the cells which it covered and from which it has been stripped, whilst the section discloses the presence of a membrane of cellulose intimately associated with the cuticle. In Table I a number of analyses of the crude cuticle are given, the analyses for the material from the younger leaves being given first.

<div align="center">TABLE I.</div>

<div align="center">*Analyses of cuticle from the leaves of* Agave americana.</div>

Source.	Carbon.	Hydrogen.	Oxygen.	Ash. Per cent.
	Per cent. on ash-free dry material.			on dry material.
Kew...................... {	58·6	8·9	32·5	3·7
	60·5	9·3	30·2	3·9
	62·4	9·4	28·2	2·1
South Africa.........	64·4	9·3	26·3	4·9

Extraction.—In a typical series of extractions, 300 g. of material were boiled with water in an open vessel during 3 hours and the light yellow solution was decanted off and filtered. After three such extractions the water was no longer coloured and the combined filtrates were evaporated to dryness, when they left a brown, crisp residue (yield 9 g. = 3%). By continuing the extraction in an autoclave under pressure at 140° a further quantity of extract was

obtained identical with the preceding one (yield 21 g. = 7%). This extract, although readily soluble in water once it had been isolated, was persistently retained by the cuticle and could only be completely removed after repeated extractions. The cuticle, dried at room temperature, was next extracted four or five times with absolute alcohol under reflux during 24 hours, by which time the extraction was complete. Removal of the solvent by distillation left a hard, yellow wax (yield 45 g. = 15%). Subsequent extractions with benzene and chloroform, and with alcohol under pressure, removed only traces of the material. The removal of cellulose, which forms a continuous layer on the under side of the cuticle lamella, was effected by solution in cuprammonium hydroxide. This was best carried out by suspending the cuticle in a 20% solution of ammonia containing a quantity of copper turnings and drawing a current of air through the solution. In this manner, the liquid is continually agitated and the solution of the cellulose thereby accelerated. When the ammonia solution had developed an intense blue colour, it was filtered off through glass wool, and the residual cuticle submitted to a further similar treatment. After five such treatments all the cellulose had been removed, for microchemical tests with chlor-zinc-iodide on sections of the residual material showed no trace of blue coloration. The combined filtrates were acidified with acetic acid. The flocculent, white precipitate which separated out was filtered off, thoroughly washed with hot water, and dried. On drying, the precipitate became discoloured and finally formed hard, black granules which could only be powdered with difficulty (yield 42 g. = 14%). The residue, *cutin*, after being washed with dilute hydrochloric acid and hot water and then dried, was obtained as a thin, dark-brown, elastic tissue. Photomicrographs of the cutin, in surface view and section, are shown in Figs. 3 and 4. Comparison of these with the corresponding photographs of the raw cuticle shows that, whilst the treatment with solvents has removed the cellulose membrane, the imprint of cell-structure on the cutin persists, an indication of the tough and resistant character of the material.

Examination of the Extracts.

Water-soluble Material.—The aqueous solution, which readily frothed on shaking, reduced Fehling's solution and formed a precipitate with basic lead acetate, but only produced a faint green coloration with neutral ferric chloride. Tannin material was not therefore present in any quantity. From its composition and properties the material appeared to consist principally of glucosides of the saponin type (Found : C, 48·7; H, 6·7; ash, 28·8%).

Alcohol-soluble Material.—A portion of the yellow solid was ground with purified sand and extracted in a Soxhlet successively with light petroleum, ether, acetone, and chloroform, each extraction lasting 24 hours. Light petroleum removed 28% of material, the more soluble portion of which responded to the phytosterol colour reaction. The ether-soluble portion, 53%, consisted of a mixture of free acids and saponifiable material and was not further examined (Found : C, 79·1; H, 13·1; ash, 0·8%).

Cuprammonia-soluble Material.—This extract was ground with a small quantity of concentrated sulphuric acid and poured into excess of water, making approximately a 5% acid solution. After being maintained at 90° for 12 hours, the yellow solution was filtered to remove a small quantity of insoluble material, neutralised with barium carbonate, filtered, and concentrated under reduced pressure. The yellow syrupy residue failed to crystallise when washed with small quantities of glacial acetic acid or after heating with 3% hydrochloric acid and again concentrating. When warmed with ammonium molybdate and dilute acetic acid, the residue gave the intense blue colour characteristic of fructose. The original extract boiled with concentrated hydrochloric acid strongly coloured aniline acetate paper, showing the presence of furfuraldehyde (Found : C, 44·1; H, 6·4; ash, 2·0%).

Examination of Cutin.

The composition of the residual cutin, after exhaustive treatment with the solvents previously mentioned, attained a constant value within the limits of experimental error, as shown by the following analyses on samples taken from various batches.

TABLE II.

Analyses of purified cuticle, or cutin, from the leaves of Agave americana.

Batch.	Carbon.	Hydrogen.	Oxygen.	Ash. Per cent.
	Per cent. on ash-free dry material.			on dry material.
1	68·8	10·2	21·0	2·0
3	69·0	10·3	20·7	3·4
4	69·1	10·2	20·7	2·9

Treatment with Alcoholic Potash.—The cutin was boiled with excess of 3% alcoholic potash under reflux during 24 hours, and the dark red solution then filtered off. After four such treatments, the residue was thoroughly washed with water, dried and weighed. From three batches of cutin of 100, 150, and 300 g., the residues amounted to 7·5, 10·2, and 23·8, respectively, or approximately 7%. The composition of the residue, as shown in Table III, was

nearly constant and almost identical with that of the cutin. It follows, therefore, that the composition of the material resolved by the alcoholic potash must also approximate to this value.

TABLE III.

Analyses of cutin residues after treatment with alcoholic potash.

Batch.	Carbon.	Hydrogen.	Oxygen.	Ash. Per cent. on dry material.
	Per cent. on ash-free dry material.			
1	67·1	8·7	24·2	31·9
3	69·1	9·8	21·1	31·3
4	68·9	9·5	21·6	31·0

From the combined alcoholic filtrates, after removal of the solvent, there was obtained a dark brown residue which readily dissolved in hot water to a clear red solution, but which on cooling became turbid and could only be filtered with difficulty. By the addition of excess of solid sodium chloride, however, a voluminous brown precipitate separated and could be filtered. The light red filtrate contained the potassium salts readily soluble in water. The residue, having been washed once with cold water, and the filtrate added to the previous one, was repeatedly boiled with water and filtered hot until a test portion of the filtrate gave no precipitate with hydrochloric acid. This solution contained the potassium salt sparingly soluble in water. The residue contained the potassium salt insoluble in water.

Acids from Potassium Salts Soluble in Water.—The filtrate was acidified with hydrochloric acid and the yellow, semi-liquid precipitate filtered off and dissolved in ether. The ethereal solution was washed, dried, and the solvent removed, leaving a brown semi-liquid mass. The corresponding potassium salts were obtained by boiling a solution of the mixed acids in absolute alcohol under reflux with excess of solid potassium carbonate until no more carbon dioxide was evolved. The cold alcoholic solution was filtered from excess of potassium carbonate, and the corresponding copper salts were obtained as a copious green precipitate by the addition of a slight excess of copper sulphate solution. The precipitate, which was insoluble in water, acetone and chloroform, was repeatedly digested with small quantities of hot absolute alcohol and filtered until the filtrate was no longer coloured. The copper salt insoluble in alcohol consisted of a light green powder, whereas the copper salt soluble in alcohol, when freed from solvent, was obtained as a dark green syrup.

The acid from the insoluble copper salt was obtained as a light brown semi-liquid mass by decomposing a chloroform suspension of the salt with hydrogen sulphide, filtering off the precipitated

copper sulphide, and evaporating the solution to dryness. It was insoluble in water and boiling light petroleum, fairly soluble in cold alcohol, chloroform, and benzene, readily so on warming (yield *ca.* 10% of the total acids obtained) (Found : C, 69·0; H, 9·9. Calc. for $C_{13}H_{22}O_3$: C, 69·0; H, 9·7%).

The *silver* salt was obtained as a copious white precipitate by the addition of a slight excess of silver nitrate to a neutral solution of the ammonium salt. When dried, it formed a dark red powder (Found : C, 45·8; H, 6·4; Ag, 31·9. $C_{13}H_{21}O_3Ag$ requires C, 46·8; H, 6·3; Ag, 32·4%).

The acid from the soluble copper salt was obtained in a similar manner by passing a stream of hydrogen sulphide through an alcoholic solution of the salt. It consisted of a yellow, semi-liquid mass and amounted to approximately 65% of the total weight of acids obtained. This acid therefore represents the chief product of saponification of cutin. Its solubility in different organic liquids was almost identical with that of the acid from the insoluble copper salt (Found : C, 68·8, 68·8; H, 10·6, 10·5; M, ebullioscopic in alcohol, 438, 479, 479. Calc. for $C_{26}H_{50}O_6$: C, 68·1; H, 10·9%; M, 458).

The *silver* salt, prepared from a neutral solution of the ammonium salt, formed a flocculent, white precipitate which darkened on drying (Found : C, 55·1; H, 8·8; Ag, 19·1. $C_{26}H_{49}O_6Ag$ requires C, 55·2; H, 8·7; Ag, 19·1%).

Acid from Potassium Salt sparingly soluble in Water.—The filtrate was acidified with hydrochloric acid and the light yellow precipitate filtered off, washed and dried. From hot chloroform it separated as a coarse, yellow, crystalline mass, m. p. 90—95°. Repeated crystallisations from this solvent failed appreciably to raise the melting point. The acid was finally purified by dissolving in boiling water, in which it was fairly soluble, and from which, after filtering and cooling, it separated as a fine, white, crystalline powder, m. p. 107—108°. Considerable loss occurred during the purification, but the yield of crude acid amounted to approximately 10% of the total acids obtained. The acid was only sparingly soluble in light petroleum, ether, or chloroform, but readily soluble in alcohol (Found : C, 62·9; H, 10·4; M, ebullioscopic in alcohol, 414; M, in camphor by Rast's method, 374. Calc. for $C_{19}H_{38}O_6$: C, 62·9; H, 10·5% *; M, 362).

The *silver* salt was prepared from a neutral solution of the ammonium salt and was finally dried at 110° (Found : C, 48·6; H, 8·5; Ag, 26·3. $C_{19}H_{37}O_6Ag$ requires C, 48·6; H, 7·9; Ag, 23·0%).

* For phloïonic acid, crystallised from water, Gilson gives C, 63·0; H, 9·9%.

The *ethyl* ester was prepared by saturating an alcoholic solution of the acid with dry hydrogen chloride and pouring the product into excess of water. The copious white precipitate which separated was filtered off, dissolved in ether, the ethereal solution washed, dried, and the solvent removed. The ester was readily soluble in alcohol and ether, less soluble in light petroleum and benzene. By allowing a solution of the ester in ether to evaporate spontaneously, the ester separated in rosettes of needles, m. p. 66—67° (Found : C, 66·9; H, 11·6; M, ebullioscopic in alcohol, 405; M, in camphor, 417. $C_{21}H_{42}O_6$ requires C, 64·6; H, 10·8%; M, 390).

Acid from Potassium Salt insoluble in Water.—The residue was suspended in dilute sulphuric acid and after some hours the flocculent, white precipitate was filtered off, washed and dried. From boiling light petroleum a flocculent, white precipitate separated on cooling, m. p. 88—90°. The small quantity obtained did not admit of further purification (Found : C, 77·4; H, 12·8%).

The separation of these four acids by fractional distillation of their methyl esters in a high vacuum was attempted, but considerable decomposition occurred during the heating and this method of separation was therefore abandoned.

Microchemical Reactions.

A number of microchemical tests were carried out in conjunction with the macrochemical work. The crude cuticle was tested for tannin by treating sections with dilute solutions of ferrous sulphate and potassium dichromate, but no coloration could be detected. Similarly, negative results were obtained by immersing sections in an alcoholic solution of phloroglucinol, washing, and subsequently treating with dilute hydrochloric acid, so that the absence of lignin can be presumed.

With solutions of chlor-zinc-iodide, or with solutions of iodine in potassium iodide after previous treatment with 70% sulphuric acid, the cuticle lamella developed a light brown colour and was sharply differentiated from the underlying layer of cellulose, which was coloured blue. After exhaustive treatment with cuprammonia in the large-scale experiments, sections of the residue showed no trace of blue colour when treated with this reagent.

In concentrated sulphuric or hydrochloric acid, the cellulose layer was rapidly destroyed, whereas the cuticle layer, even after long standing, was apparently unaltered.

With 1% solutions of Sudan III, using the method described by Lee and Priestley (*Ann. Bot.*, 1924, **38**, 528), the cuticle lamella was stained a deep red, the cellulose layer being unaffected. This

stain has recently been used in microchemical technique for the detection of fats and waxes, but it was found that the exhaustively purified cutin stained just as readily with this reagent as did the original cuticle, and, even after prolonged treatment with alcoholic potash, whereby the majority of the cutin was resolved, the residue persisted in colouring with this stain. Sudan III is a useful microchemical reagent for staining cuticle and cutin, but this fact does not appear to justify the inclusion of the latter material under the term " fat " or " wax," since cutin is quite insoluble in solvents in which fats and waxes ordinarily dissolve.

CXCII.—*The Spatial Structure of cycloParaffins. Part I. A New Aspect of Mohr's Theory and the Isomerism of Decahydronaphthalene.*

By WILFRED ALAN WIGHTMAN.

THE recent isolation of two isomeric forms of decahydronaphthalene, which appear to stand in a *cis*- and *trans*-relationship, has definitely shown that a rigid planar conception of the structure of such compounds is no longer tenable (Hückel, *Nach. K. Ges. Wiss. Göttingen*, 1923, 43; *Annalen*, 1925, **441**, 1). It was shown by Sachse (*Ber.*, 1890, **23**, 1363; *Z. physikal. Chem.*, 1892, **10**, 203; 1893, **11**, 185) that strain in the Baeyer sense (*i.e.*, deviation from the tetrahedral angle) can be eliminated from a non-planar structure having more than five carbon atoms in the ring, and further, that two such strain-free configurations are possible in the case of cyclohexane (Fig. 1). These ideas were developed by Mohr (*J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316), who postulated further that the temporary strain involved in a conversion of Sachse's strain-free structures one into the other is sufficiently slight to be over-

come merely by the forces due to molecular collisions. He also predicted the isomerism of decahydronaphthalene.

The principal objection to the acceptance of Sachse's structures

FIG. 1.
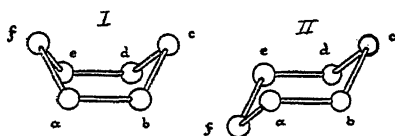
FIG. 2.
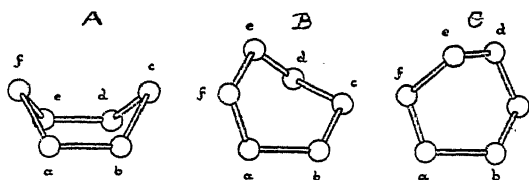
FIG. 3.
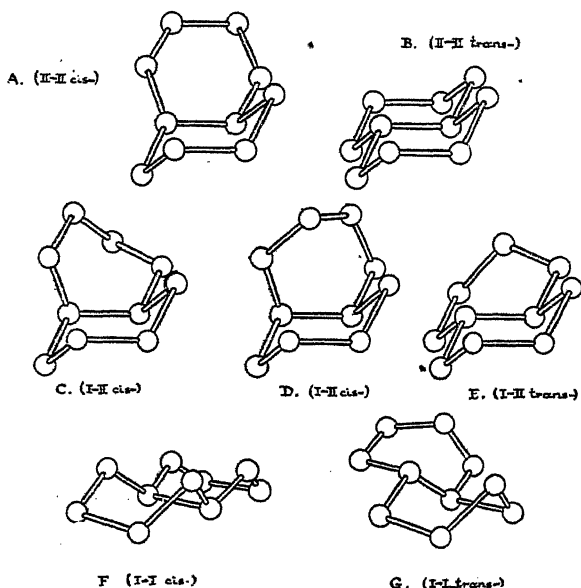
Possible isomerides of decahydronaphthalene.

as stable configurations is the large number of isomerides they would require. For whilst all the carbon atoms of type II are obviously equivalent, this is not the case with type I, and the latter, if static, requires the existence (*e.g.*) of several monosubstituted

*cyclo*hexanes. It is of interest, however, to determine whether co-ordinated relative rotations about the single bonds are possible without strain, and to examine the consequences of such a phenomenon; to this end, the author has constructed models in which these mechanical requirements are fulfilled.

The models show (*a*) that type II is a rigid structure and cannot pass into type I (or any other form) without strain, and (*b*) that type I is a " loose " structure which, although it cannot without strain be transformed into type II, is capable, by strain-free relative rotations of its carbon atoms, of passing through a series of forms which annihilate the isomeric possibilities above mentioned. Fig. 2 shows three of the configurations it can assume when the sphere (*b*) is clamped; the motion of (*a*) and (*c*) is rotatory only, whilst that of (*d*), (*e*) and (*f*) is both rotatory and translatory. If more than one sphere is fixed, the motion is completely arrested. The atoms (*c*) and (*f*) in A are equivalent to (*a*) and (*d*) in B and to (*e*) and (*b*) in C—hence the absence of isomerism. There still remains, however, the possibility of there being two *cyclo*hexanes (I and II), unless we accept Mohr's postulate.

In the case of decahydronaphthalene, Mohr showed that the theory of strain-free structures requires two isomerides incapable of interconversion by any means short of rupturing bonds. These he formulated as B and F (Fig. 3). For reasons which will presently appear, it has been thought advisable to set out all the possible combinations of pairs of the two types of strainless ring (Fig. 3). (A, C, D, and E have optical isomerides which are not shown.) All forms involving type II of the *cyclo*hexane ring are rigid : F and G are capable of strain-free rotations, but are not interconvertible —this has been confirmed by models. Inspection of the models reveals further that by applying the Mohr postulate all the *cis*-forms can be reduced to F and all the *trans*-forms to G, so that the existence of strainless motion makes no difference to the number of isomerides required by Mohr's theory.

There is one more consequence of strainless motion, however, to which attention may be directed. The effect of molecular collisions upon type I, where such motion is possible, is much less likely to cause transformation into the other type than in the case of type II, where there is no alternative. The existence of type I is therefore favoured at the expense of type II, and it seems likely that *cyclo*hexane and its derivatives may conform to type I exclusively. The existence of this type alone is sufficient to explain all the established facts and requires the existence of two (but only two) decahydronaphthalenes.

Since these ideas were developed by the author, Zelinsky (*Ber.*,

1924, **57**, 2062) has announced the isolation of a third isomeride of decahydronaphthalene. It has therefore seemed desirable to publish the above detailed examination of the isomeric possibilities of this substance, in view of the probability that the existence of more than two isomerides will lead to the abandonment of the Mohr postulate.

The author is indebted to Professor C. K. Ingold, F.R.S., for his interest and helpful criticism, and to Mr. Neville Warr for his aid in the design and construction of the models.

CXCIII.—β-*Piperonylpropionitrile and Some Derived Substances.*

By WILSON BAKER and ROBERT ROBINSON.

LAPWORTH and McRAE (J., 1922, **121**, 1699) found that aromatic aldehydes condense with sodium cyanoacetate in aqueous solution to give excellent yields of arylidenecyanoacetic acids, and Baker and Lapworth (J., 1924, **125**, 2333) have shown that these substances may be reduced by sodium amalgam and water to saturated acids which can be decomposed with formation of β-arylpropionitriles. We have prepared by these means large quantities of β-piperonylpropionitrile (I), the transformations of which are the subject of this communication. On nitration in acetic acid solution, the nitrile yields its 6-*nitro*-derivative (II) and this is changed by reduction with tin and a mixture of acetic and hydrochloric acids into a *methylenedioxydihydrocarbostyril* (III).
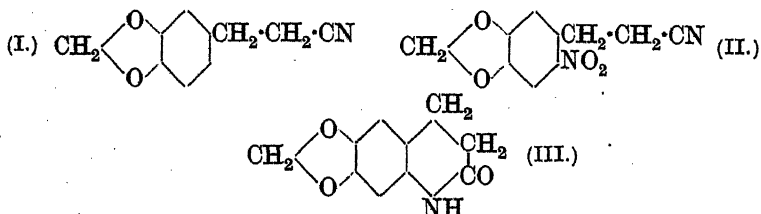
No direct synthesis of safrole has been recorded and one object of our work was to effect the transformation

$$R·CHO \longrightarrow R·CH_2·CH:CH_2.$$
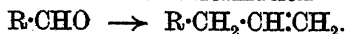
In this we were unsuccessful, but we are able to record a new synthesis of *iso*safrole. β-Piperonylpropionitrile is readily reduced by means of sodium and alcohol to γ-*piperonylpropylamine*, $CH_2O_2:C_6H_3·CH_2·CH_2·CH_2·NH_2$ (IV), the overall yield of this base

from piperonal being no less than 50%. From it, on treatment with methyl iodide and alcoholic sodium ethoxide, the quaternary *ammonium iodide*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3{]}I$ (V), was produced and this was transformed to the related hydroxide which it was hoped could be decomposed with formation of safrole, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH{:}CH_2$. However, under all conditions, the product was *iso*safrole, $CH_2O_2{:}C_6H_3{\cdot}CH{:}CH{\cdot}CH_3$ (compare Senfter and Tafel, *Ber.*, 1894, **27**, 2309). The acetyl derivative of (IV) was prepared, but it was not found possible to dehydrate it to a ring homologue of 1-methyl*nor*hydrastinine (D.R.-P. 235,358) (compare Braun and Bartsch, *Ber.*, 1912, **45**, 3389).

β-Piperonylpropionitrile shows no tendency to yield a hydrindene derivative under the influence of hydrogen chloride and, under the conditions of the Hoesch synthesis, reacts with resorcinol, ultimately forming homopiperonylresacetophenone (VI). This suggested that an attempt should be made to gain further information regarding

(VI.)   (VII.)
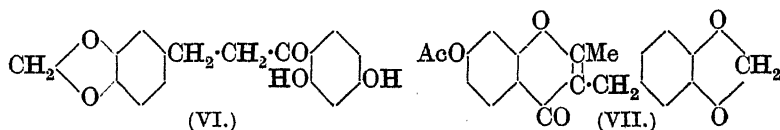
the course of the synthesis of *iso*brazilein trimethyl ether salts (Crabtree and Robinson, J., 1918, **113**, 864) by the action of boiling formic acid, in presence of zinc chloride, on homoveratrylpaeanol. Two schemes seem the most plausible, the intermediate being in (A) an indene derivative and in (B) a chromone derivative.
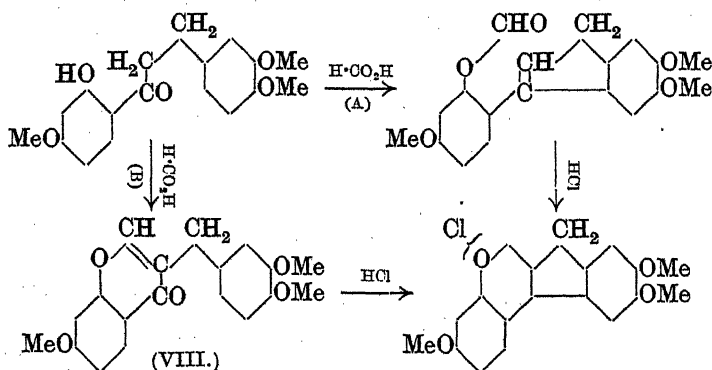
(VIII.)

Chromone derivatives of the type VIII have now been prepared, the first stage being the acetylation of the phenolic ketone (VI) by boiling acetic anhydride in presence of sodium acetate; the acetoxyhomopiperonylmethylchromone (VII) thus obtained is

hydrolysed and methylated. The whole process has been repeated starting with veratraldehyde instead of piperonal, yielding, finally, 7-methoxy-3-homoveratryl-2-methylchromone (IX). This substance shows some tendency to pass into an *iso*brazilein derivative, but its behaviour is such that it cannot possibly be regarded as an intermediate in the synthesis of the salt (X) (compare Crabtree and Robinson, *loc. cit.*).
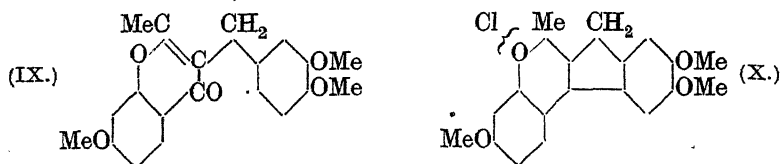
These experiments certainly exclude scheme (B) given above and therefore favour the view that scheme (A) is correct.

Mention should be made of the interesting dimorphism exhibited by some of these chromone derivatives, since the persistence of the phenomenon despite changes in the vicinity of position 7 in the nucleus indicates the existence of some molecular property common to the different members of the series.

Another matter of general interest encountered in the course of our work concerns a remarkable bromination mechanism. It is known that many pyrones, *e.g.*, 2 : 3-dimethylchromone (Petschek and Simonis, *Ber.*, 1913, **46**, 2014; Simonis and Elias, *Ber.*, 1915, **48**, 1499), form coloured, unstable dibromides which on boiling with water revert to the original chromone derivative and bromine. This behaviour was at first regarded as a proof of the ethylene character of pyrones, although later the dibromides were considered to be oxonium compounds.

7-Methoxy-3-homopiperonyl-2-methylchromone (XI) forms a dibromide in acetic acid solution. The bromine is loosely held, since the substance liberates iodine from potassium iodide and, on boiling with water, some bromine is evolved. On boiling with alcohol, however, a bromo-derivative (XIII) of the original chromone is produced. This substance is stable to hot alkalis and by treatment with hydrogen bromide in acetic acid solution cannot be reconverted into the dibromide. It is obvious that the bromine in the dibromide is associated with the pyrone nucleus and that on boiling with alcohol one of the bromine atoms enters an aromatic nucleus—most likely in the position indicated. The pyrone nucleus is regarded as a dipole (Heilbron, Barnes, and Morton, J., 1923, **123**, 2564; compare Armit and Robinson, in the press) and the most acceptable formulation of the dibromides is illustrated in the expression (XII) in the particular case under discussion.

MeC CH$_2$ (XI.) MeO

Br Me CH$_2$ OBr (XII.) MeO

MeC CH$_2$ CO Br (XIII.) MeO
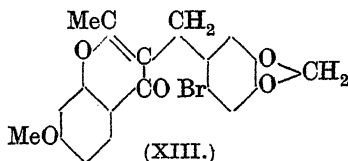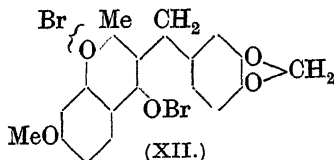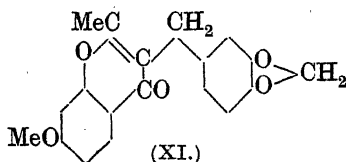
Thus we conceive the reaction as an intramolecular rearrangement of the kation of a pyrylium bromide. It is favoured by the polarising effect of the chromone dipole on the bromine and by the proximity in space of a bromine atom, which has a tendency to separate with a positive charge, to an unsaturated centre which has a tendency to acquire a negative charge.

EXPERIMENTAL.

β-*Piperonylpropionitrile* (I) was obtained from α-cyano-β-piperonylpropionic acid (Piccinini, *Atti R. Accad. Sci. Torino*, 1904, **39**, 121; Baker and Lapworth, *loc. cit.*) by thermal decomposition in presence of copper powder (compare Willstätter and Pummerer, *Ber.*, 1904, **37**, 3745; Rinkes, *Rec. trav. chim.*, 1920, **39**, 205). The acid (45 g.) and washed copper bronze (10 g.) were rapidly heated over a free flame in a distilling flask of about 250 c.c. capacity. A very lively evolution of gas set in and ceased suddenly in about a minute. A further quantity (45 g.) of the acid was introduced and this also decomposed and the resulting nitrile distilled. A colourless oil (50 g.), b. p. 186—187°/18—20 mm., and a pale yellow, higher-boiling fraction (6 g.) were obtained. After several months a sample crystallised at once when it was disturbed. The substance may be obtained in large, well-developed prisms, m. p. 33°, by adding light petroleum to a concentrated ethereal solution (Found : C, 68·7; H, 5·2; N, 8·1. C$_{10}$H$_9$O$_2$N requires C, 68·5; H, 5·2; N, 8·0%). The nitrile is readily soluble in most organic solvents and dissolves in sulphuric acid to a deep crimson solution which, when diluted with a little water and gently heated, becomes olive-green. By treatment with a warm alkaline solution of hydrogen peroxide (Radziszewski, *Ber.*, 1885, **18**, 355) it was readily converted into the known β-piperonylpropionamide, m. p. 123·5° (Decker, *Annalen*, 1913, **395**, 289; Borsche and Eberlein, *Ber.*, 1914, **47**, 1469), which was also isolated as the result of an experiment made with the object

of closing the hydrindene ring by acting on the nitrile in dry ethereal solution with hydrogen chloride.

β-6-*Nitropiperonylpropionitrile* (II) was obtained by addition of nitric acid (1 c.c.; d 1·42) to a solution of β-piperonylpropionitrile (2·5 g.) in acetic acid (25 c.c.). After 15 minutes, the mixture was added to water (200 c.c.) and the crystals (2·3 g.) were collected; they crystallised from alcohol in pale honey-coloured, flat needles, m. p. 113° (Found : C, 54·5; H, 3·7; N, 12·9. $C_{10}H_8O_4N_2$ requires C, 54·5; H, 3·7; N, 12·7%). On heating with dilute aqueous sodium hydroxide, ammonia is evolved and a deep crimson solution produced. The methylenedioxy-group is hydrolysed in all probability, since the product gives an olive-green coloration with ferric chloride. There was also evidence of an attack on the methylenedioxy-group during the course of acid hydrolysis. A mixture of β-6-nitropiperonyl-propionitrile (2 g.) and concentrated hydrochloric acid (100 c.c.) was boiled for 18 hours. On cooling, the filtered solution deposited yellow plates (0·9 g.) which, after crystallisation from alcohol, had m. p. 153—153·5° (Found : C, 50·2; H, 4·0; N, 6·0. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·8; N, 5·9%). This substance is therefore β-6-*nitropiperonylpropionic acid*. The mother-liquors from several preparations were concentrated to a small bulk, filtered from some of the acid just described, and extracted with ether. The yellow, crystalline residue, left on removal of the solvent, gave an olive-green colour with ferric chloride and appeared to be a mixture containing about 60% of a catechol derivative. β-6-Nitropiperonyl-propionitrile (3 g.) was dissolved in warm acetic acid (45 c.c.), and tin (10 g.) and concentrated hydrochloric acid (10 c.c.) were added; after 12 hours, hydrochloric acid (5 c.c.) was introduced and the mixture heated on the steam-bath until the reaction was complete. The tin was eliminated as sulphide from the hot, diluted solution, and the acetic acid by boiling. The neutralised solution deposited small crystals (1·3 g.) and the substance was recrystallised from alcohol (charcoal) in colourless plates which softened at 227° and melted at 230° (Found : C, 62·9; H, 4·8; N, 7·5. Calc., for $C_{10}H_9O_3N$, C, 62·8; H, 4·8; N, 7·3%). The substance has feebly basic properties and appears to be identical with the ethylamidopiperonyl-ω-carboxylic anhydride, m. p. 235° with slight previous softening, prepared by F. M. Perkin (J., 1891, 59, 159) by reduction of ethyl 6-nitropiperonylacrylate. The latter compound can be obtained from 6-nitropiperonal, a fact which establishes the orientation of the substituents.

γ-Piperonylpropylamine (IV).—In the course of 2 hours, sodium (35 g.) was added in small pieces to a boiling solution of β-piper-onylpropionitrile (17·5 g.) in absolute alcohol (350 c.c.). Water

(2 l.) was added and the base extracted with ether, the dried solution being distilled. 15·3 G. of a colourless liquid, b. p. 160—161°/14 mm., were obtained (yield 85%).

γ-Piperonylpropylamine is a highly refracting liquid, $d_{16°}^{16°}$ 1·141, having a weak basic odour. It is sufficiently soluble in water to impart a strong alkaline reaction and on exposure to air gives a solid *carbonate*, m. p. 92—94°. The *hydrochloride* crystallises from alcohol in long, colourless, silky needles, m. p. 206—208° (Found : C, 55·8; H, 6·7; N, 6·5; Cl, 16·3. $C_{10}H_{14}O_2NCl$ requires C, 55·7; H, 6·6; N, 6·5; Cl, 16·4%). The *acetyl* derivative,

$$CH_2O_2{:}C_6H_3{\cdot}[CH_2]_3{\cdot}NH{\cdot}COMe,$$
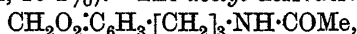
obtained by the action of acetic anhydride on the base, crystallises from water or from benzene in colourless needles, m. p. 89° (Found : N, 6·4. $C_{12}H_{15}O_3N$ requires N, 6·3%).

Piperonylidene-γ-piperonylpropylamine,

$$CH_2O_2{:}C_6H_3{\cdot}[CH_2]_3{\cdot}N{:}CH{\cdot}C_6H_3{:}O_2CH_2,$$
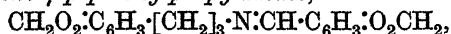
was prepared by heating a mixture of the amine (5 g.) and piperonal (4·2 g.) on the steam-bath for 30 minutes. The crystalline mass obtained on cooling was dissolved in warm acetone; the filtered solution deposited colourless, glistening plates, m. p. 79·5° (Found : N, 4·5. $C_{18}H_{17}O_4N$ requires N, 4·5%). The derivative is readily soluble in organic solvents with the exception of light petroleum.

γ-*Piperonylpropyltrimethylammonium Iodide* (V).—A freshly-prepared solution of sodium ethoxide (2 mols.) in alcohol (45 c.c.) was added to a mixture of γ-piperonylpropylamine (10 g.; 1 mol.), alcohol (25 c.c.), and methyl iodide (15 c.c.), and the whole was gently heated, when the quaternary salt (13 g.) crystallised. Ether was added to the mother-liquor, and the mixture of sodium iodide and the quaternary ammonium iodide which separated was collected. On standing in the air, the former deliquesced, leaving the latter unchanged (2 g.). The *iodide* crystallises from alcohol in colourless, shining plates, m. p. 146° (Found : I, 36·4. $C_{13}H_{20}O_2NI$ requires I, 36·4%). The iodide (10 g.) was converted into hydroxide by means of an excess of freshly precipitated silver oxide in presence of water (50 c.c.), the strongly alkaline filtrate was concentrated on the steam-bath under diminished pressure, and the syrupy residue was decomposed by gradually raising the temperature to 160°, water, trimethylamine, and a little *iso*safrole being carried over. The distillate and residue were combined, acidified with dilute sulphuric acid, and distilled in steam. The oil was collected from the distillate by ether, and 2·77 g. of *iso*safrole were obtained. The yield from the iodide is 60% and the overall yield from piperonal is 24%. The substance was identified by its b. p. and characteristic picrate,

red needles, m. p. 73·5—74° (Found : N, 10·9.   Calc. for $C_{16}H_{13}O_9N_3$, N, 10·8%) as ordinary *trans-iso*safrole.   The m. p. of the picrate was not depressed by admixture with an authentic specimen (compare Hoering and Baum, *Ber.*, 1909, **42**, 3076; Nagai, *J. Coll. Eng. Tokyo Imp. Univ.*, 1921, **11**, 83 in reference to isomeric *iso*safroles).

Homopiperonylresacetophenone (VI).—A solution of β-piperonyl-propionitrile (20 g.) and resorcinol (25 g.) in dry ether (80 c.c.) was saturated at 0° with hydrogen chloride and kept at 0° for 48 hours, ether (50 c.c.) being added when half this time had elapsed.   The ketimine hydrochloride separated as a yellow, crystalline crust, which was washed with ether and decomposed by heating with water during 30 minutes on the steam-bath.   The *ketone* crystallised on standing and was crushed, washed, and dried (15·8 g.).   The ethereal mother-liquor deposited a fresh crop of ketimine hydrochloride on dilution with fresh ether, and the ketone from this was purified by solution in aqueous sodium hydroxide, a further 4 g. being ultimately isolated.   The substance crystallises from hot aqueous methyl alcohol in colourless, shining plates, m. p. 130° (Found : C, 67·1 ; H, 5·0. $C_{16}H_{14}O_5$ requires C, 67·1 ;   H, 4·9%).   Homopiperonyl-resacetophenone is readily soluble in ether, the simple alcohols, and benzene, and dissolves to some extent in hot water.   When heated with acetic anhydride and zinc chloride, it gives a solution which exhibits an intense, yellowish-green fluorescence, doubtless owing to the production of a salt of the *iso*brazilein series.

Homopiperonylpaeanol,*   CH₂⟨O⟩... CH₂·CH₂·CO... HO⟨⟩OMe·—
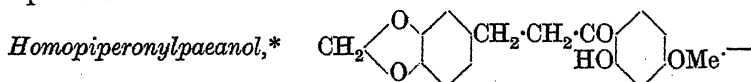
The foregoing phenol was shaken in aqueous sodium hydroxide with methyl sulphate, when the *monomethyl* ether separated even from the alkaline solution.   The substance crystallises from methyl alcohol in colourless needles, m. p. 89—90° (Found : C, 67·9 ; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0;   H, 5·4%).   The phenolic function is very weak (compare the case of benzylpaeanol; Crabtree and Robinson, *loc. cit.*), although an alcoholic solution develops a reddish-violet coloration with ferric chloride.   When heated with acetic anhydride and zinc chloride, it gives a red solution exhibiting intense ivy-green fluorescence.   No chromone derivative could be obtained by the action of acetic anhydride and sodium acetate on the substance.   It appears to be a general rule that paeanol derivatives cannot be converted into chromones by acetic anhydride, whereas the corresponding resacetophenones undergo the reaction

* Tognazzi (*Gazzetta*, 1924, **54**, 697) has obtained this substance by the catalytic reduction of piperonylidenepaeanol.   The m. p. quoted is 85—87°.

(as shown below in the present instance) smoothly and often with the production of excellent yields.

7-*Hydroxy*-3-*homopiperonyl*-2-*methylchromone* (corresponding with VII).—The acetyl derivative described below (5 g.) was hydrolysed by boiling dilute aqueous sodium carbonate until solution occurred (2·5 hours), and the filtered solution was acidified with hydrochloric acid. The colourless, crystalline precipitate was dried (4·07 g.), and recrystallised from ethyl alcohol, separating in small, colourless, silky needles (Found : C, 69·4; H, 4·7. $C_{18}H_{14}O_5$ requires C, 69·7; H, 4·6%). The solution in aqueous or alcoholic sodium hydroxide exhibits a bluish-violet fluorescence. Prepared as described, the substance is obtained in the α-form, m. p. 214—215°, then solidifying, and melting at 222—223° (β-form). The α-form was obtained from either modification of the acetyl derivative, but on one occasion the pasty mass of needle crystals of the α-variety changed to small, well-formed prisms. These consisted of the β-form, m. p. 222—223°, and could be recrystallised unchanged from alcohol. A mixture of both forms melted at 222—223°. If a hot alcoholic solution of the α-form is seeded with the β-form, slow crystallisation gives the pure β-form, but rapid cooling causes the separation of a mixture.

The *acetyl* derivative (VII) was obtained in excellent yield when a mixture of homopiperonylresacetophenone (5 g.), anhydrous sodium acetate (5 g.), and acetic anhydride (20 c.c.) was heated at 180° for 15 hours. The solid (6·2 g.) obtained by decomposition with dilute hydrochloric acid crystallised from alcohol containing a little water in colourless needles, m. p. 101·5° (Found : C, 68·3; H, 4·4. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The yield of hydroxyhomopiperonylmethylchromone from homopiperonylresacetophenone is 93% of that theoretically possible. This acetyl derivative also is dimorphous and the relation between the two forms resembles that existing between those of the related phenol. The modification directly obtained is the α-form, and this solidifies almost immediately after melting and then melts at 119·5°. As before, this β-variety is the more stable and transformation of the supercooled compound into the α-form could not be accomplished by seeding, although the change from α to β could readily be brought about. In one case only, the β-form was obtained directly from the preparation and had m. p. 119·5°, unaltered by crystallisation. Both varieties crystallise in needles and the change β to α has not been observed.

The *methyl* ether (XI), obtained by shaking the phenol dissolved in alcoholic potassium hydroxide with methyl sulphate, crystallised from methyl alcohol in small, colourless prisms, m. p. 124—125°

(Found : C, 70·0; H, 5·1. $C_{19}H_{16}O_5$ requires C, 70·3; H, 5·0%). Under a great variety of conditions this substance can be made to yield fluorescent solutions by treatment with powerful acid condensing agents, but it was found impossible to isolate any tangible quantities of definite oxonium salts of the *iso*brazilein type. The greater part of the material was always converted into insoluble, pink solids which could not be crystallised.

Dibromide of the Methyl Ether (XII).—7-Methoxy-3-homopiperonyl-2-methylchromone (2 g.; 1 mol.) dissolved in acetic acid (20 c.c.) was treated with a 10% acetic acid solution of bromine (1 mol.), when yellow crystals at once began to separate; after 30 minutes, these were collected, washed with acetic acid, and dried (2·8 g.; 93%) (Found : Br, 33·1. $C_{19}H_{16}O_5Br_2$ requires Br, 33·1%). The ochre-yellow powder becomes orange on keeping, and on boiling with acetic acid a pink solution with green fluorescence is produced. The melting point is indefinite; darkening commences at about 155°, and at about 167° the substance is almost black and softens, finally melting to a deep red liquid above 170°. The solution in sulphuric acid is reddish-purple, but rapidly becomes brown, grey, olive-green and then brown again. On boiling the dibromide (1 g.) with alcohol (100 c.c.) for 30 minutes, a pink, faintly fluorescent solution is produced and, on cooling, this deposits faintly pink, small needles (0·72 g.), m. p. 206—207° (Found : C, 56·6; H, 3·9; Br, 19·7. $C_{19}H_{15}O_5Br$ requires C, 56·6; H, 3·8; Br 19·8%). This substance, probably XIII, is stable to hot alcoholic potassium hydroxide for a short time and when heated with zinc chloride and acetic anhydride gives a carmine solution with intense yellowish-green fluorescence. Cyclisation by treatment with activated magnesium in dry *iso*amyl-ethereal solution could not be effected.

α-*Cyano-β-veratrylacrylic acid* was obtained from veratraldehyde in quantitative yield by an application of the method of Lapworth and McRae (*loc. cit.*). The pale yellow needles obtained on acidification of the solution were dried, and crystallised from hot water or from ethyl alcohol in thin, pale yellow, microscopic needles, m. p. 201—202° (Found : C, 61·4; H, 4·8; equiv., 232·3. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·8%; equiv., 233·1). The acid crystallises from methyl alcohol in lustrous, long needles of a greyish-violet colour and having a metallic appearance. The substance contains solvent of crystallisation (Found : equiv., 264·3. $C_{12}H_{11}O_4N,CH_4O$ requires equiv., 265·2) and on exposure to the air the crystals become opaque, yellow, and friable. The peculiar appearance is due to fluorescence and it may be noted that the related ethyl ester exhibits blue fluorescence in the crystalline state (Kauffmann, *Ber.*, 1919, 52, 1422).

α-Cyano-β-veratrylpropionic Acid.—The reduction of the acrylic acid was carried out as described by Baker and Lapworth (*loc. cit.*), the weight of the saturated acid obtained being equal to that of the original veratraldehyde. It crystallised from benzene in bunches of needles, m. p. 139° (Found : C, 61·1 ; H, 5·5 ; equiv., 236·3. $C_{12}H_{13}O_4N$ requires C, 61·3 ; H, 5·6% ; equiv., 235·1).

β-*Veratrylpropionitrile*, $\begin{smallmatrix}MeO\\MeO\end{smallmatrix}\bigg\langle\ \ \bigg\rangle CH_2\cdot CH_2\cdot CN$.—This substance and all those described below were obtained by the methods already recorded for the piperonyl analogues. The nitrile was obtained in 70% yield as a very pale yellow oil, b. p. 194—195°/17 mm., which crystallised and could be recrystallised from ether–ligroin in colourless prisms, m. p. 46·5° (Found : C, 68·9 ; H, 6·8. $C_{11}H_{13}O_2N$ requires C, 69·1 ; H, 6·9%).

Homoveratrylresacetophenone, obtained in poor yield (22%), crystallised from methyl alcohol, in which it was sparingly soluble, in colourless needles, m. p. 146—147° (Found : C, 67·2 ; H, 5·9. $C_{17}H_{18}O_5$ requires C, 67·5 ; H, 6·0%).

7-Acetoxy-3-homoveratryl-2 methylchromone separates from ethyl alcohol in colourless, tabular parallelipipeda, m. p. 140·5° (Found : C, 68·4 ; H, 5·5. $C_{21}H_{20}O_6$ requires C, 68·5 ; H, 5·5%).

7-Hydroxy-3-homoveratryl-2-methylchromone, obtained in 90% yield from homoveratrylresacetophenone, crystallises from hot, aqueous ethyl alcohol in small, glistening plates, m. p. 183— 184° (Found : C, 69·8 ; H, 5·6. $C_{19}H_{18}O_5$ requires C, 69·9 ; H, 5·6%). The alkaline solutions of this chromone exhibit blue fluorescence.

7-Methoxy-3-homoveratryl-2-methylchromone (IX) separates from methyl alcohol in colourless, obliquely truncated, four-sided prisms, m. p. 108° (Found : C, 70·3 ; H, 5·8. $C_{20}H_{20}O_5$ requires C, 70·5 ; H, 5·9%). This substance was prepared because it was thought that formaldehyde from the methylenedioxy-group might vitiate the results of experiments on the condensation of the piperonyl analogue. When it was boiled with acetic anhydride and zinc chloride, there was evidence that some *iso*brazilein derivative was produced, but the yield was very small.

CXCIV.—*Synthetical Experiments in the* iso*Quinoline Group. Part I.*

By ROBERT DOWNS HAWORTH *and* WILLIAM HENRY PERKIN, jun.

IN the course of experiments on the constitution and synthesis of the berberine alkaloids, which have occupied much of the attention of these laboratories during the last few years, a large number of new derivatives of *iso*quinoline have been prepared which were not included in the previous publications, partly in order to economise space and partly because they did not lead directly to the synthesis of these alkaloids or their derivatives. Since, however, these new substances have an interest of their own and may very probably prove to be useful in other synthetical work, we have decided to publish a brief account of their preparation and properties. The first of these papers had for its central idea the synthesis of berberine alkaloids from 6 : 7 : 2′ : 3′-*tetramethoxy-2-benzyl*-1 : 2 : 3 : 4-*tetra-hydro*iso*quinoline* (I) derivatives by the introduction of a carbon atom between the positions 1 and 6′, thus :
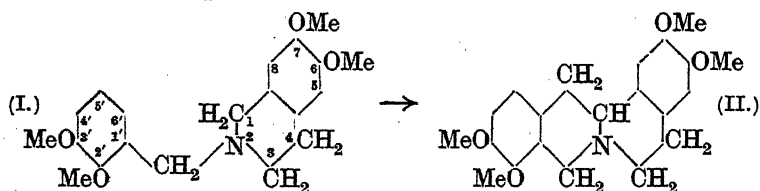
Derivatives of (I) can be obtained from 6 : 7-dimethoxy*iso*-quinoline and 2 : 3-dimethoxybenzyl bromide, which readily combine to give the iso*quinolinium bromide* (III), from which the corresponding ψ-*base* (IV), ψ-*cyanide* (V), iso*quinolone* (VI), and *tetra-hydro*iso*quinoline* (I) have been prepared. Several attempts have
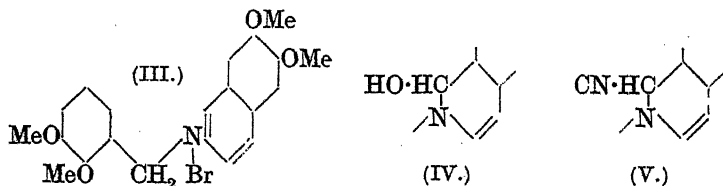
been made to convert 6 : 7 : 2′ : 3′-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (I) into the berberine type (II), but without success. Thus methylal and acetal had no action on the tetrahydro*iso*quinoline and, although Schneider and Schröter (*Ber.*, 1920, **53**, 1459) have shown that sulphoacetic acid converts papaverine into coralyne (VII), it does not react with the tetrahydro*iso*quinoline (I). The substance (I) was next oxidised

to the *dihydro*iso*quinolinium iodide* (VIII), from which the corresponding ψ-*base* (IX), ψ-*cyanide* (X) and iso*quinolone* (XI) have been obtained.

(VI.) (VII.) (VIII.)

(IX.) (X.) (XI.)
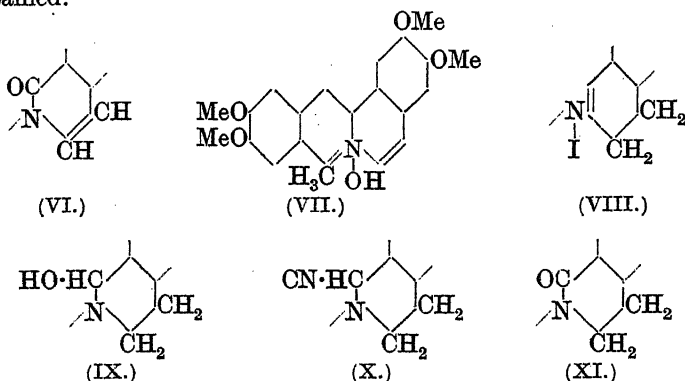
The remaining stages of the research had for their object the conversion of the substances (VIII–XI) into the corresponding 1-aldehydo- or 1-carboxy-tetrahydro*iso*quinoline derivatives, as it seemed likely that these might be useful in synthesising the required berberine or corydaline structure. The first method investigated depends on the fact that, as was first shown by Hope and Robinson (J., 1911, 99, 2114), ψ-bases condense with aliphatic nitro-compounds, and we found that the ψ-base (IX) readily yields a nitromethyl derivative (XII) on treatment with nitromethane. It was hoped that reduction of this derivative would lead to the formation of an oxime and that the aldehyde (XIII), obtained from this, would readily lose water, giving a substance (XIV) of the dihydroberberine type.

(XII.) (XIII.) (XIV.)

(XV.) (XVI.)
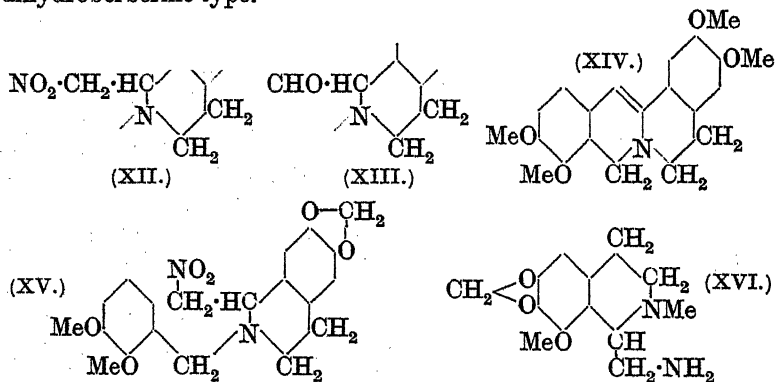
All experiments in this direction have been unsuccessful owing to the elimination of methylamine during reduction and formation

of the ψ-base (IX), and it was also observed that 6 : 7-*methylenedioxy-2′ : 3′ - dimethoxy - 2 - benzyl - 1 - nitromethyl* - 1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (XV) behaves similarly towards reducing agents. On the other hand, anhydrocotarnine-nitromethane was reduced to anhydrocotarnine-methylamine (XVI) in both acid and alkaline solutions. We have also attempted to close the ring with the aid of the cyano-group of the ψ-cyanide (X) and the hydrogen of the 6-position by means of dry hydrogen chloride, but, in spite of the careful exclusion of moisture, the ψ-cyanide was always, to a large extent, converted into the corresponding quaternary ammonium salt and no internal condensation took place.

In some cases, partial hydrolysis occurred with formation of small quantities of *tetramethoxybenzyltetrahydro*iso*quinolinecarboxylamide* (XVII). Other experiments showed that the instability of the ψ-cyanide is so pronounced that it is unsuitable for synthetical purposes and attempts to oxidise it to the more stable 1-cyano*iso*quinolinium iodide were unsuccessful. Again, although the ψ-cyanide (X) reacts with magnesium methyl iodide with the formation of *tetramethoxybenzylmethyltetrahydro*iso*quinoline* (XVIII), the attempt to oxidise this base to the corresponding dihydro*iso*quinolinium iodide led only to the formation of an uninviting substance, which showed no sign of possessing a reactive methyl group capable of condensing with nitrosodimethylaniline or of conversion into the aldehydo-group by other means.

(XVII.) $NH_2 \cdot CO \cdot HC$ ... CH_2 / N / CH_2

$CH_3 \cdot HC$ ... CH_2 / N / CH_2 (XVIII.)

(XIX.) MeO / MeO ... $N \cdot COPh$ / $CH \cdot CN$

MeO / MeO ... N / $CO \cdot NH_2$ (XX.)
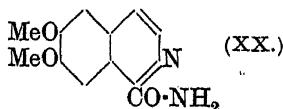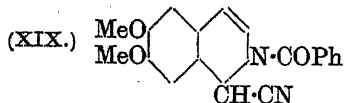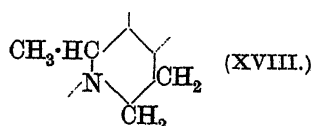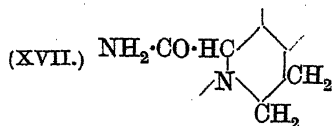
An investigation into the conditions for the preparation of 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid has led to interesting results. Reissert (*Ber.*, 1905, **38**, 3427) showed that 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline could be obtained by the action of potassium cyanide and benzoyl chloride on *iso*quinoline. Starting with 6 : 7-dimethoxy*iso*quinoline, we have prepared *dimethoxy-cyanobenzoyldihydro*iso*quinoline* (XIX) in a similar manner and find that it is readily hydrolysed by hydrogen chloride to benzaldehyde and dimethoxy*iso*quinolinecarboxylamide (XX).

This amide condenses with 2 : 3-dimethoxybenzyl bromide, and the product, on reduction, yields an acid amide which is identical

with the amide (XVII) obtained by the action of hydrogen chloride on the ψ-cyanide (X).

This amide could, however, not be hydrolysed to the corresponding acid, and, unfortunately, we have failed to find a method for condensing the $-CO \cdot NH_2$ group of the amide with the hydrogen atom in the 6′-position which would have resulted in a substance containing the berberine structure.

EXPERIMENTAL.

The 2 : 3-dimethoxybenzaldehyde used in the following experiments was prepared by the methylation of *o*-vanillin by means of methyl sulphate and methyl-alcoholic potassium hydroxide. During the preparation of large quantities of this substance, a small quantity of an oil was isolated which was insoluble in sodium hydrogen sulphite and yielded 2 : 3-dimethoxybenzaldehyde on warming with dilute acids. This oil distilled at 134—136°/11 mm. and proved to be 2 : 3 - *dimethoxybenzaldehyde dimethylacetal*, $(MeO)_2C_6H_3 \cdot CH(OMe)_2$ (Found : C, 62·3; H, 7·6. $C_{11}H_{16}O_4$ requires C, 62·3; H, 7·5%). 2 : 3-Dimethoxybenzyl alcohol was prepared from the aldehyde by the action of alcoholic potassium hydroxide under the conditions described by Doutteau (*Bull. Soc. chim.*, 1912, **11**, 653).

2 : 3-*Dimethoxybenzyl bromide* was obtained by dissolving the alcohol (30 g.) in dry benzene (250 c.c.), cooling in a freezing mixture, and saturating with hydrogen bromide. The excess of hydrogen bromide was removed by calcium carbonate, the whole filtered, the residue washed with benzene, the filtrate and washings were dried over potassium carbonate, the benzene was removed, and the residue rapidly distilled under reduced pressure.

This distillation is necessary in order to free the bromide from a dark coloured impurity. The distillate solidified on cooling and melted at about 27—29° (Found : Br, 34·0. $C_9H_{11}O_2Br$ requires Br, 34·6%).

This bromide possesses very powerful lachrymatory properties and produces violent sneezing. It dissolves in the usual solvents and slowly undergoes hydrolysis in the presence of moist air.

6 : 7 : 2′ : 3′-*Tetramethoxy-2-benzylisoquinolinium Bromide* (III).— The 6 : 7-dimethoxy*iso*quinoline employed in this research was obtained by the fusion of xanthaline with potassium hydroxide under the conditions described by Dobson and Perkin (*J.*, 1911, **99**, 137). This substance (9 g.) and 2 : 3-dimethoxybenzyl bromide (11 g.) were allowed to react in dry benzene (50 c.c.), and after remaining over-night, the *iso*quinolinium bromide was collected and washed with benzene, when an almost quantitative yield was obtained (Found : C, 57·4; H, 5·2; Br, 19·0. $C_{20}H_{22}O_4NBr$ requires C, 57·1;

H, 5·2; Br, 19·0%). This bromide is readily soluble in water, ethyl and methyl alcohols, and acetone, but sparingly soluble in ether or benzene. It separates from ether–alcohol in long, colourless needles which soften at 109° and melt to a pale yellow liquid at 114°. When a crystal is dissolved in concentrated sulphuric acid, bromine is liberated, the solution becomes colourless on warming, and the addition of a drop of nitric acid produces a blood-red coloration. The corresponding *iodide* is precipitated when potassium iodide is added to an aqueous solution of the bromide and separates from methyl alcohol in large, colourless, rhombic prisms, m. p. 204—205° (Found : I, 27·0. $C_{20}H_{22}O_4NI$ requires I, 27·2%). On addition of iodine in potassium iodide to the aqueous solution of the bromide (III), a *periodide* is precipitated which separates from alcohol in slender, green needles, m. p. 159—160°. When this is shaken with dilute sulphurous acid, it is converted into the *iso*quinolinium iodide.

1 - *Hydroxy* - 6 : 7 : 2′ : 3′-*tetramethoxy* - 2 - *benzyl* - 1 : 2 - *dihydro*iso - *quinoline* (IV).—When a large excess of sodium hydroxide was added to the aqueous solution of the bromide (III), the ψ-base (IV) slowly separated as a thick, gelatinous precipitate which was collected, washed with water, and dried in an evacuated desiccator (Found : C, 67·0; H, 6·6. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%). This ψ-base is a colourless, amorphous substance readily soluble in dilute acids and is reprecipitated by sodium hydroxide but not by ammonia or potassium acetate. It is readily soluble in the usual organic solvents, and solutions in alcohol or benzene undergo oxidation to the corresponding *iso*quinolone (VI) on exposure to air. The colourless solution of the ψ-base in concentrated sulphuric acid becomes blood-red on the addition of a drop of nitric acid.

A *stannous chloride* derivative is precipitated on adding a solution of stannous chloride to the solution of the ψ-base in dilute hydrochloric acid. It crystallises from water in elongated prisms, m. p. 163—164°, and yields the amorphous ψ-base on decomposition by hydrogen sulphide.

1 - *Cyano* - 6 : 7 : 2′ : 3′- *tetramethoxy* - 2 - *benzyl* - 1 : 2 - *dihydro*iso - *quinoline* (V).—When a concentrated solution of potassium cyanide was added to an aqueous solution of the *iso*quinolinium bromide (III), the ψ-*cyanide* (V) separated as an oil which rapidly solidified. This, after being thoroughly dried in an evacuated desiccator, separated from benzene in small needles, m. p. 120—122° (Found : N, 7·7. $C_{21}H_{22}O_4N_2$ requires N, 7·6%).

This ψ-cyanide is soluble in alcohol, chloroform, or nitrobenzene, but sparingly soluble in benzene or petroleum. It dissolves with decomposition in water and is reprecipitated on the addition of

potassium cyanide. It rapidly loses hydrogen cyanide in the presence of moisture or dilute acids.

6 : 7 : 2' : 3'-*Tetramethoxy-2-benzyl*-1-iso*quinolone* (VI).—(i) The *iso*quinolinium bromide (III ; 2 g.) was dissolved in water (40 c.c.) and potassium hydroxide (1 g.), and the solution oxidised by potass-ium ferricyanide (4·5 g.) in water (20 c.c.). After boiling for a few minutes, the mixture was cooled, when the *iso*quinolone separated in almost theoretical yield. (ii) The *iso*quinolinium bromide (III; 2 g.), dissolved in alcohol (15 c.c.), was boiled for $\frac{1}{2}$ hour with a 50% solution of potassium hydroxide (10 c.c.). Most of the alcohol was removed by distillation, the residue diluted with water, and the crude brown *iso*quinolone recrystallised from methyl alcohol. This *iso*quinolone separates from methyl alcohol in colourless prisms, m. p. 171°. It is slightly soluble in ether, benzene, or alcohol in the cold, readily soluble in hot alcohol or benzene, and is a weak base, dissolving in glacial acetic acid or concentrated mineral acids and being reprecipitated on dilution with water (Found : C, 67·5; H, 5·9; N, 3·8. $C_{20}H_{21}O_5N$ requires C, 67·6; H, 5·9; N, 3·9%).

6 : 7 : 2' : 3' - *Tetramethoxy* - 2 - *benzyl* - 1 : 2 : 3 : 4 - *tetrahydro*iso - *quinoline* (I).—The bromide (III; 5 g.), dissolved in alcohol (150 c.c.) and concentrated hydrochloric acid (150 c.c.), was boiled with a large excess of granulated tin for 6 hours. Most of the alcohol was removed by distillation under reduced pressure, and the residual liquid decanted into water (4 vols.), when a tin double salt separated which was collected and decomposed by hydrogen sulphide. The filtrate from the tin sulphide was concentrated and sodium hydroxide added, when the *tetrahydro*iso*quinoline* separated as an oil which rapidly solidified (3 g.) (Found : C, 69·6; H, 7·3. $C_{20}H_{25}O_4N$ requires C, 69·9; H, 7·3%).

This tetrahydro*iso*quinoline is readily soluble in benzene, chloro-form, or acetone, sparingly soluble in ether or petroleum, and crystallises from methyl alcohol in colourless prisms, m. p. 112—113°. The solution in concentrated sulphuric acid becomes blood-red on the addition of a drop of nitric acid.

The *stannous chloride* derivative separates from hot water in small plates, m. p. 109—110°. The base was recovered after heating for an hour with methylal or acetal and also after heating with sulphoacetic acid under the conditions employed by Schneider and Schröter (*loc. cit.*).

6 : 7 : 2' : 3'- *Tetramethoxy* - 2 - *benzyl* - 3 : 4 - *dihydro*iso*quinolinium Iodide* (VIII).—The tetrahydro*iso*quinoline (I; 2·5 g.) was dissolved in alcohol (25 c.c.) containing potassium acetate (1 g.), and the solution boiled during the gradual addition of a 10% solution of iodine in alcohol (18 c.c.). Most of the alcohol was removed

distillation, and the residue treated with sulphurous acid, when the *isoquinolinium iodide* separated as a mass of yellow crystals (2·7 g.). It crystallised from boiling alcohol in fine, yellow rhombs melting at 200° to a red liquid (Found : C, 51·2; H, 5·2. $C_{20}H_{24}O_4NI$ requires C, 51·2; H, 5·2%). This iodide is sparingly soluble in alcohol or water in the cold, but readily soluble on boiling.

1 - *Hydroxy* - 6 : 7 : 2′ : 3′ - *tetramethoxy* - 2 - *benzyl* - 1 : 2 : 3 : 4 - *tetra* - *hydro*isoquinoline (IX).—The iodide (VIII) was converted into the corresponding chloride by boiling for 1 hour with water and freshly-precipitated silver chloride, and the filtrate concentrated, cooled, and made strongly alkaline with sodium hydroxide. The white, amorphous precipitate of the *ψ-base* (IX) was collected, dissolved in dilute hydrochloric acid, reprecipitated with sodium hydroxide, thoroughly washed, and dried in a desiccator (Found : C, 66·3; H, 7·0. $C_{20}H_{25}O_5N$ requires C, 66·8; H, 7·0%).

The *ψ*-base (IX) is soluble in ether, benzene, chloroform, acetone, or alcohol, and sparingly soluble in petroleum. Attempts to obtain it in the crystalline condition were unsuccessful. The alcoholic solution exhibits a green fluorescence and the solution in concentrated sulphuric acid becomes blood-red on the addition of nitric acid. The *picrate* was prepared by adding picric acid to the alcoholic solution of the *ψ*-base and separated from alcohol in bright yellow needles, m. p. 135° (decomp.).

The *zinc chloride* derivative separated as a yellow gum when a solution of zinc chloride was added to a solution of the *ψ*-base in dilute acetic acid. The gum was dissolved in hot methyl alcohol and allowed to cool slowly, when the double salt crystallised in large, pale yellow, truncated octahedra, m. p. 158—160°.

6 : 7 : 2′ : 3′-*Tetramethoxy* - 2 - *benzyl* - 3 : 4 - *dihydro* - 1 - iso*qu inolone* (XI).—This was prepared by boiling an alcoholic solution of the dihydro*iso*quinolinium iodide (VIII) with excess of 50% potassium hydroxide for 1 hour. The mixture was cooled and poured into water, when a red oil separated. The liquid was decanted, the oil washed with dilute hydrochloric acid and boiled with methyl alcohol, from which the substance separated in colourless prisms, m. p. 160° (Found : C, 67·2; H, 6·4. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%). This *iso*quinolone is readily soluble in alcohol, ether, or benzene and almost insoluble in petroleum. It dissolves in glacial acetic acid and in concentrated mineral acids, but is reprecipitated on dilution with water.

6 : 7 : 2′ : 3′-*Tetramethoxy*-2-*benzyl*-1-*nitromethyl*-1 : 2 : 3 : 4-*tetra*-*hydro*isoquinoline (XII).—The dihydro*iso*quinolinium iodide (VIII; 2·3 g.) was dissolved in warm methyl alcohol (15 c.c.) containing nitromethane (1 g.), a methyl-alcoholic solution of potassium

hydroxide (0·5 g.) slowly added, the mixture cooled and allowed to remain over-night, and the *nitromethyl* derivative, which had separated, washed with water. It crystallised from methyl alcohol in slender needles, m. p. 111—112° (Found : C, 62·5; H, 6·5; N, 6·9. $C_{21}H_{26}O_6N_2$ requires C, 62·7; H, 6·5; N, 7·0%).

This nitromethyl derivative is soluble in hot alcohol, benzene, or chloroform, sparingly soluble in ether, and still less soluble in petroleum. It dissolves in dilute acids and is reprecipitated on the addition of ammonia or potassium acetate. When a solution in moderately concentrated acid is heated, a salt of the ψ-base is produced. A sodium salt is formed when sodium methoxide is added to a methyl-alcoholic solution of the nitromethyl derivative, and a clear solution is obtained on diluting with water. The action of reducing agents—such as stannous chloride, zinc dust and sodium hydroxide, sodium amalgam in acid, alkaline, or neutral solution, or colloidal palladium and hydrogen—led, in all cases, to the elimination of methylamine and regeneration of the ψ-base.

6 : 7 - *Methylenedioxy* - 2' : 3'- *dimethoxy* - 2 - *benzyl* - 1 - *nitromethyl* - 1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (XV).—Norhydrohydrastinine was prepared from *N*-formylhomopiperonylamine by Decker's method (D.R.-P. 245025). Molecular proportions of this substance and 2 : 3-dimethoxybenzyl bromide were allowed to react at the ordinary temperature for 12 hours in benzene solution, when the quaternary ammonium bromide separated as a brown, crystalline mass. This was dissolved in methyl alcohol and left over-night with nitromethane (1·5 mols.) and potassium hydroxide (2 mols.); the nitromethyl derivative was then collected, washed with water, and crystallised from much alcohol, from which it separated in small needles, m. p. 135—136° (Found : C, 62·0; H, 5·7. $C_{20}H_{22}O_6N_2$ requires C, 62·1; H, 5·7%). It is explained on p. 1436 that attempts to reduce this substance to the corresponding oxime were again unsuccessful.

1-*Cyano*-6 : 7 : 2' : 3'-*tetramethoxy*-2-*benzyl* - 1 : 2 : 3 : 4 - *tetrahydro*-so*quinoline* (X).—When a concentrated solution of potassium cyanide was added to an aqueous solution of the dihydroiso*quinol*-inium iodide (VIII), the ψ-*cyanide* (X) rapidly separated as a white, crystalline precipitate, which crystallised from alcohol in brilliant, cubic crystals, m. p. 125° (Found : C, 68·4; H, 6·5; N, 7·4. $C_{21}H_{24}O_4N_2$ requires ·C, 68·5; H, 6·5; N, 7·6%). This ψ-cyanide is readily soluble in benzene, chloroform, or warm alcohol, sparingly soluble in ether or petroleum. The alcoholic solution exhibits a green fluorescence and the cyanide is rapidly converted into salts of the dihydroiso*quinolinium* type (VIII) by mineral acids. When an ethereal solution of iodine is added to the benzene solution of

the ψ-cyanide, a black periodide is precipitated which is converted into the dihydro*iso*quinolinium iodide (VIII) by the action of sulphurous acid.

6 : 7 : 2′ : 3′ - *Tetramethoxy* - 2 - *benzyl* - 1 - *methyl*- 1 : 2 : 3 : 4 - *tetra-hydro*isoquinoline (XVIII).—A solution of the ψ-cyanide (X ; 1 mol.) in anisole was added to an anisole solution of magnesium methyl iodide (3 mols.), when a yellow precipitate was produced which became grey on warming on the water-bath for an hour. The mixture was decomposed with dilute hydrochloric acid, and the hydriodide of the base, which separated as an oil, decomposed by potassium hydroxide to the corresponding base. This could not be obtained in the crystalline condition, but the *picrate*, prepared by adding picric acid to an alcoholic solution of the base, separated from alcohol in needles, m. p. 157—158° (Found : C, 55·1 ; H, 5·4. $C_{21}H_{27}O_4N,C_6H_3O_7N_3$ requires C, 55·3 ; H, 5·1%). The base was liberated from the picrate by the action of ammonia as an oil and, on oxidising the alcoholic solution of the base with iodine, oily products were obtained which did not condense with nitrosodimethylaniline (p. 1436).

1-*Cyano*-6 : 7-*dimethoxy*-2-*benzoyl*-1 : 2-*dihydro*isoquinoline (XIX). —6 : 7-Dimethoxy*iso*quinoline (22 g.) was mixed with aqueous potassium cyanide (300 c.c. of 10%) and shaken with benzoyl chloride (33 g.), when a yellow colour developed and an orange semi-solid substance was gradually deposited. The liquid was decanted, the residue washed with 10% hydrochloric acid and shaken with ether, when it solidified (yield 35%). This cyano-benzoyl derivative (XIX) separates from alcohol in colourless needles, m. p. 164° (Found : C, 71·5 ; H, 5·0 ; N, 9·1. $C_{19}H_{16}O_3N_2$ requires C, 71·2 ; H, 5·0 ; N, 8·7%).

1 - *Cyano* - 6 : 7 : 2′ : 3′- *tetramethoxy* - 2 - *benzoyl* - 1 : 2 - *dihydro*iso-quinoline.—2 : 3-*Dimethoxybenzoyl chloride* was prepared by heating the acid (20 g.) with a slight excess of thionyl chloride, the excess was removed by distillation, and the crude oil, which slowly solidified, condensed with 6 : 7-dimethoxy*iso*quinoline (11 g.) and 10% potassium cyanide solution (150 c.c.). The product (12 g.) solidified rapidly and was crystallised from glacial acetic acid, from which it separated in needles, m. p. 181° (Found : C, 65·8 ; H, 5·4. $C_{21}H_{20}O_5N_2$ requires C, 66·3 ; H, 5·3%).

6 : 7-*Dimethoxyiso*quinoline-1-*carboxylamide* (XX).—This was obtained by the action of hydrogen chloride on either of the cyano-benzoyl derivatives described above. The cyano-benzoyl derivative (XIX ; 3·5 g.) was dissolved in dry chloroform, cooled in a freezing mixture, and saturated with dry hydrogen chloride, when the solution became yellow, a green fluorescence developed, and, after

some time, a mass of orange needles separated. These were washed with ether, suspended in water, and distilled in steam, when benzaldehyde was removed. The residue was filtered from traces of impurity, made alkaline with ammonia, and the precipitate (1·5 g.) collected, washed with water, and crystallised from alcohol, separating in long needles, m. p. 168—169° (Found : C, 62·1; H, 5·2; N, 11·8. $C_{12}H_{12}O_3N_2$ requires C, 62·1; H, 5·2; N, 12·0%). This amide (XX) is readily soluble in hot water and, on the addition of mercuric chloride, a double compound separates which crystallises from hot water in long, colourless needles. The amide cannot be hydrolysed to the corresponding acid either by acids or alkalis, but a small amount of the acid was obtained from the ammoniacal mother-liquors of the above preparation, by rendering faintly acid with acetic acid and adding copper acetate, when a pale green copper salt separated. On decomposition with hydrogen sulphate, this yielded a small quantity of 6 : 7-dimethoxy*iso*quinoline-1-carboxylic acid identical with the acid obtained by Goldschmiedt (*Monatsh.*, 1885, **6**, 964; 1887, **8**, 520) by the oxidation of papaverine. The mercuric chloride derivative of this acid is sparingly soluble in water, from which it separates in small needles.

6 : 7 : 2′ : 3′ - *Tetramethoxy - 2 - benzyl - 1 : 2 : 3 : 4 - tetrahydroiso - quinoline-1-carboxylamide* (XVII).—The ψ-cyanide (X; 1·5 g.) was dissolved in freshly distilled anisole (30 c.c.), containing fused zinc chloride (2 g.) in suspension, and the solution saturated with dry hydrogen chloride, the temperature being maintained below 15°. A brown gum separated on the zinc chloride and, after 3 hours, most of the solvent was decanted, the gum dissolved in hot water, and the last traces of anisole were removed in a current of steam. The residue was mixed with a solution of ammonia and ammonium chloride, the pale yellow solid collected and crystallised from benzene, from which the amide separated in colourless needles, m. p. 192°.

The yield varied in different experiments from nothing to about 25% of the theoretical, and the exact conditions for successful preparation could not be determined. In all the experiments much of the ψ-cyanide (X) was converted into the dihydro*iso*quinolinium chloride of type (VIII). A more trustworthy method for the preparation of the amide (XVII) is the following : Equimolecular proportions of 2 : 3-dimethoxybenzyl bromide and 6 : 7-dimethoxy-*iso*quinoline-1-carboxylamide (XX) are boiled for 24 hours in toluene solution, when the ammonium bromide separates as a brown, crystalline powder which does not melt at 250° (Found : Br, 17·0. $C_{21}H_{23}O_5N_2Br$ requires Br, 17·2%).

This bromide is reduced by boiling in much alcohol with a large excess of granulated tin and hydrochloric acid for 12 hours, the

alcohol is removed by distillation and the residue poured into water, when a sticky tin double salt separates. This is suspended in boiling water and decomposed by hydrogen sulphide. The filtrate, made alkaline by ammonia, deposits the amide (XVII), which is then recrystallised from benzene (Found : C, 64·9 ; H, 6·7 ; N, 7·3. $C_{21}H_{26}O_5N_2$ requires C, 65·3 ; H, 6·7 ; N, 7·3%).

This amide dissolves readily in dilute acids, but, even after boiling with concentrated hydrochloric acid or alcoholic potassium hydroxide, it can be recovered unchanged.

Anhydrocotarnine-methylamine (XVI).—Anhydrocotarnine-nitromethane (5 g.) was dissolved in methyl alcohol containing sodium methoxide (Na = 1 g.) and poured into a 30% solution of sodium hydroxide (50 c.c.). The clear solution was heated at 60° and zinc dust (40 g.) added in small portions during 2 hours. The mixture was extracted with ether, the extract dried over potassium carbonate and the solvent removed, when a pale yellow oil remained which decomposed on distillation. The *dihydrochloride*, precipitated on saturating the ethereal solution of the base with dry hydrogen chloride, is readily soluble in water and alcohol and can be crystallised from alcohol–ether in long needles, m. p. 227° (Found : N, 8·6 ; Cl, 21·4. $C_{13}H_{20}O_3N_2Cl_2$ requires N, 8·7 ; Cl, 21·9%).

The *picrate*, prepared by adding picric acid to the alcoholic solution of the base, is sparingly soluble and melts at 200° (decomp.). Anhydrocotarnine-methylamine may also be obtained by reducing anhydrocotarnine-nitromethane with stannous chloride and hydrochloric acid in the cold.

THE DYSON PERRINS LABORATORY,
        OXFORD.   [*Received, April 28th*, 1925.]

CXCV.—*Synthetical Experiments in the* iso*Quinoline Group. Part II.*

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun., and JOHN RANKIN.

IN Part I of this series (preceding paper) an account has been given of an unsuccessful attempt to achieve a synthesis of alkaloids of the berberine group from 6 : 7 : 2′ : 3′-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and its derivatives. The earlier stages of this investigation were rendered difficult because of the limited supply of *o*-vanillin at our disposal, and it was therefore thought advisable that a series of experiments similar to those described in Part I should first be carried out with the more accessible ordinary vanillin. The present communication contains

an account of the preparation and properties of the substances studied during this investigation.

3 : 4-*Dimethoxybenzyl Bromide.*—3 : 4-Dimethoxybenzyl alcohol, prepared by the action of alcoholic potassium hydroxide on 3 : 4-dimethoxybenzaldehyde (Tiffeneau, *Bull. Soc. chim.*, 1911, 9, 929), dissolved in eight times its weight of dry benzene, was saturated with dry hydrogen bromide at 10°, the product neutralised by calcium carbonate, filtered, and the benzene removed by distillation under reduced pressure. The colourless oil remaining could not be distilled under reduced pressure owing to decomposition with loss of hydrogen bromide and formation of a green substance, but, after remaining in an evacuated desiccator for several days, it slowly solidified (Found : Br, 33·9. $C_9H_{11}O_2Br$ requires Br, 34·6%).

This bromide is very soluble in the usual organic solvents and is rapidly hydrolysed by moisture. It has very slight lachrymatory properties and this fact is somewhat remarkable in view of the pungent character of 2 : 3-dimethoxybenzyl bromide (p. 1437).

6 : 7 : 3' : 4'-*Tetramethoxy-2-benzyl*iso*quinolinium Bromide* (compare III).*—Equimolecular proportions of crude 3 : 4-dimethoxybenzyl bromide and 6 : 7-dimethoxy*iso*quinoline were allowed to react in benzene solution. After remaining over-night, the separation of the bromide was practically complete and the pale yellow precipitate was collected and washed with benzene. The nearly pure bromide, obtained in excellent yield, separated from water in clusters of slender needles, m. p. 137—138° (Found : C, 57·1; H, 5·5; Br, 18·7. $C_{20}H_{22}O_4NBr$ requires C, 57·1; H, 5·2; Br, 19·0%). The corresponding *iodide* was obtained by the addition of potassium iodide to the warm aqueous solution of the bromide, when a precipitate formed immediately and increased on cooling the solution. It was almost insoluble in cold and only slightly soluble in boiling water, but dissolved readily in boiling methyl alcohol and separated in long, thin, pale yellow prisms, m. p. 203—204° (Found : I, 27·1. $C_{20}H_{22}O_4NI$ requires I, 27·2%).

1 - *Hydroxy* - 6 : 7 : 3' : 4' - *tetramethoxy* - 2 - *benzyl*-1 : 2 - *dihydro*iso - *quinoline* (compare IV).—This was prepared by the addition of excess of sodium hydroxide to the cold aqueous solution of the bromide (compare III), when no immediate precipitation took place, but after some time the ψ-base separated as a colourless, flocculent precipitate. This ψ-base (compare IV) could not be recrystallised and rapidly darkened and shrank to a plastic mass

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* The formulæ of the substances described in this communication differ from those described in Part I only in the position of two methoxy-groups, and the numbers inserted here refer to the formulæ of the corresponding substances in Part I.

on exposure to air. The base, rapidly dried in an evacuated desiccator, was analysed (Found : C, 67·1 ; H, 6·2 ; N, 3·9. $C_{20}H_{23}O_5N$ requires C, 67·2 ; H, 6·4 ; N, 3·9%).

6 : 7 : 3' : 4'-*Tetramethoxy-2-benzyl-1-isoquinoline* (compare VI).— An alcoholic solution of the bromide (compare III) was heated with a large excess of alcoholic potassium hydroxide, most of the alcohol removed by distillation, and the residue diluted with water, when an oil separated. This was washed by decantation, dissolved in a large excess of boiling hydrochloric acid (20%), and a few drops of alcohol were added ; on cooling, colourless, slender needles separated, m. p. 128—129° (Found : C, 67·4 ; H, 5·9. $C_{20}H_{21}O_5N$ requires C, 67·6 ; H, 5·9%).

1-*Cyano*-6 : 7 : 3' : 4'-*tetramethoxy-2-benzyl-1 : 2-dihydro*isoquinoline (compare V).—When a solution of potassium cyanide was added to an aqueous solution of the bromide (compare III) the ψ-*cyanide* was precipitated as an oil which solidified on stirring. It was collected, washed well, and dried in a desiccator (Found : N, 7·8. $C_{21}H_{22}O_4N_2$ requires N, 7·6%).

This ψ-cyanide is readily soluble in the usual organic solvents and rapidly loses hydrogen cyanide on treatment with dilute acids. It is moderately soluble in water, from which it is reprecipitated by potassium cyanide. A small quantity of the ψ-cyanide was obtained in the crystalline state by allowing its aqueous solution to drop slowly into a very dilute solution of potassium cyanide. After standing for about 10 days, the ψ-cyanide had separated in colourless needles which darkened at 115° and melted at 117° (decomp.).

6 : 7 : 3' : 4'-*Tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydro*isoquinoline (compare I).—The bromide (compare III ; 5 g.) was dissolved in a mixture of alcohol (150 c.c.) and concentrated hydrochloric acid (150 c.c.), boiled over-night with an excess of granulated tin, the alcohol removed by distillation, and the residue decanted from the tin into water. The liquid, with the tin double salt in fine suspension, was heated to boiling, when the double salt coagulated in a form which allowed of filtration. It was suspended in boiling water, decomposed with hydrogen sulphide, the filtrate concentrated and made alkaline with sodium hydroxide, when the *tetrahydro*iso-*quinoline* was precipitated as a grey, slightly viscous solid. This (2·4 g.) crystallised from ether in colourless prisms, m. p. 93° (Found : C, 69·7 ; H, 7·3. $C_{20}H_{25}O_4N$ requires C, 70·0 ; H, 7·3%). The base is readily soluble in dilute acids and does not react with methylal, acetal, or sulphoacetic acid (compare p. 1434).

6 : 7 : 3' : 4' - *Tetramethoxy* - 2 - *benzyl* - 3 : 4 - *dihydro*isoquinolinium *Iodide* (compare VIII).—The base (compare I ; 5 g.) was dissolved in alcohol (30 c.c.), containing potassium acetate (2 g.), and heated

on the steam-bath during the addition of an alcoholic solution
of iodine (40 c.c. of 10%). Most of the alcohol was removed by
distillation and the dark brown residue treated with sulphurous
acid, when small, orange crystals separated which, after crystal-
lisation, melted at 184—185° (Found : C, 51·5; H, 5·3. $C_{20}H_{24}O_4NI$
requires C, 51·2; H, 5·1%). This iodide dissolves in boiling alcohol,
but is sparingly soluble in hot and almost insoluble in cold water.
A *periodide* was obtained as a dark brown precipitate on the addi-
tion of an alcoholic solution of iodine to an alcoholic solution of
the iodide and crystallised from anisole in small, brown needles,
m. p. 160° (Found : C, 33·7; H, 3·5; I, 52·4. $C_{20}H_{24}O_4NI_3$ requires
C, 33·2; H, 3·3; I, 52·7%). The *chloride*, prepared from the
iodide by treatment with silver chloride, separated from a little
water in large, yellow rhombs melting indefinitely at 52—56° and
containing solvent of crystallisation. The loss of weight on drying
at 120° was 15·5% and the dry substance gave C, 63·2; H, 6·5.
$C_{20}H_{24}O_4NCl$ requires C, 63·3; H, 6·3%.

1-*Hydroxy*-6 : 7 : 3′ : 4′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso-
quinoline (compare IX).—This substance separated as an amorphous
precipitate when sodium hydroxide was added to the solution of
the above chloride. It could not be obtained crystalline and
darkened on exposure to air. The corresponding iso*quinolone*
(compare XI) may be obtained by warming an alcoholic solution
of the above iodide with alcoholic potassium hydroxide, but is more
conveniently prepared in the following way. The iodide (3 g.)
and potassium hydroxide (0·75 g.) are dissolved in alcohol and
treated with a solution of potassium ferricyanide (4·25 g.) in the
minimum of water. After heating on the steam-bath for 2 hours,
most of the alcohol is removed by distillation, and the solution
extracted several times with ether. The ethereal extract is well
washed with dilute hydrochloric acid, and the ether allowed to
evaporate slowly, when the *iso*quinolone separates in large, amber,
rhombic crystals, m. p. 116° (Found : C, 67·3; H, 6·2. $C_{20}H_{23}O_5N$
requires C, 67·2; H, 6·4%).

1-*Cyano*-6 : 7 : 3′ : 4′-*tetramethoxy*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*-
iso*quinoline* (compare X).—This was prepared by the addition of a
concentrated solution of potassium cyanide to an aqueous solution
of the chloride described above. The *ψ-cyanide* was collected,
dissolved in ether, dried over potassium carbonate, and the ether
allowed to evaporate slowly, when colourless, cubic crystals
separated, m. p. 98° (Found : C, 68·3; H, 6·6; N, 7·4. $C_{21}H_{24}O_4N_2$
requires C, 68·5; H, 6·5; N, 7·6%). This *ψ*-cyanide is readily
soluble in alcohol, and the solution exhibits a green fluorescence.

6 : 7 : 3′ : 4′-*Tetramethoxy*-2-*benzyl*-1-*nitromethyl*-1 : 2 : 3 : 4-*tetra-
hydro*iso*quinoline* (compare XII).—The iodide (see above) (2·3 g.),

nitromethane (1 g.), and potassium hydroxide (0·5 g.) were allowed to react over-night in methyl-alcoholic solution (20 c.c.). The *nitromethyl* derivative, after being washed with water, separated from methyl alcohol in colourless needles, m. p. 148—149° (Found : C, 62·6; H, 6·5; N, 6·7. $C_{21}H_{26}O_6N_2$ requires C, 62·7; H, 6·5; N, 6·9%). In its behaviour with reducing agents, this nitromethyl derivative resembles the isomeric substance described in Part I (p. 1441), methylamine and a derivative of the ψ-base being produced.

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CXCVI.—*Synthetical Experiments in the* isoQuinoline *Group. Part III.*

By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

IT has been shown by Haworth, Perkin, and Rankin (J., 1924, **125**, 1685) that veratrylnorhydrohydrastinine (I), on treatment with formaldehyde and hydrochloric acid, yields a substance isomeric with tetrahydroberberine (II) and to this substance (III) the name tetrahydro-ψ-berberine was given. The present communication contains an account of some experiments which have been instituted with the object of determining whether it is possible to convert veratrylnorhydrohydrastinine into tetrahydroberberine by indirect methods.
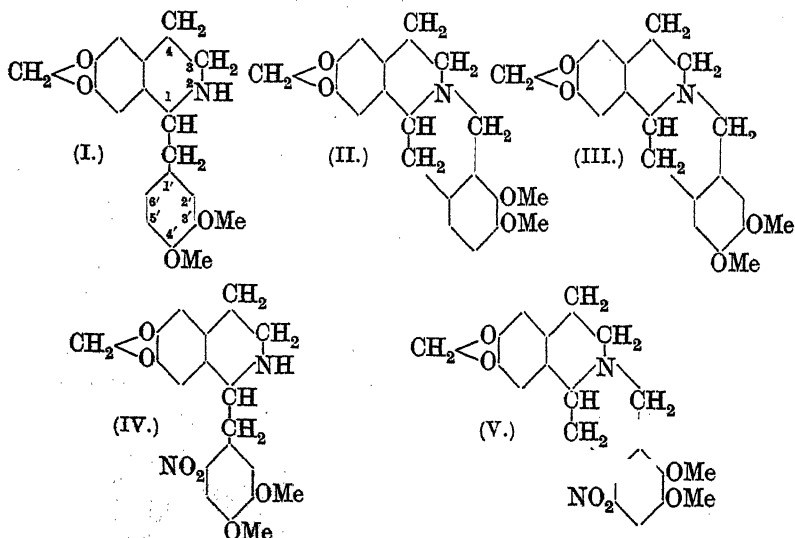
When veratrylnorhydrohydrastinine reacted, in glacial acetic acid solution, with nitric acid which had previously been treated with carbamide, a mononitro-derivative was obtained. This proved to be 6-*nitroveratrylnorhydrohydrastinine* (IV), because, on reduction with zinc dust and hydrochloric acid, an amino-derivative was obtained which gave the greenish-blue coloration with ferric chloride characteristic of *p*-anisidines.

It is clear from the consideration of the formula that this 6-nitro-derivative might conceivably yield 6-nitrotetrahydroberberine (V) on treatment with formaldehyde and hydrochloric acid. When the experiment was tried, it was found that, although the substance (IV) interacts readily with formaldehyde, the product yields no trace of nitrotetrahydroberberine on treatment with hydrochloric acid. As this failure may have been due to the well-known inhibiting effect of the nitro-group, we next carried out a similar series of experiments with the corresponding derivative of veratrylnorhydrohydrastinine containing a bromine atom in the place of the nitro-group. 6-Bromoveratrylnorhydrohydrastinine could not be obtained pure by the direct action of bromine and in order to synthesise it, 6-bromohomoveratric acid was prepared by the bromination of homoveratric acid and found to be identical with the acid which Pschorr (*Annalen*, 1912, **391**, 35) had already obtained by another process. When equimolecular proportions of homopiperonylamine and 6-bromohomoveratric acid were heated at 180°, excellent yields of 6-bromohomoveratroylhomopiperonylamine (VI) were obtained. This was treated with phosphorus oxychloride in toluene solution, and the product directly reduced with zinc and dilute sulphuric acid, when 6-*bromoveratrylnorhydrohydrastinine* (VII) was readily obtained pure and in good yield. This bromo-derivative reacted readily with formaldehyde, but bromoveratryl-norhydrohydrastinine was recovered when the condensation product was treated with hydrochloric acid and no trace of bromo-tetrahydroberberine (V, with Br for NO_2) could be isolated.
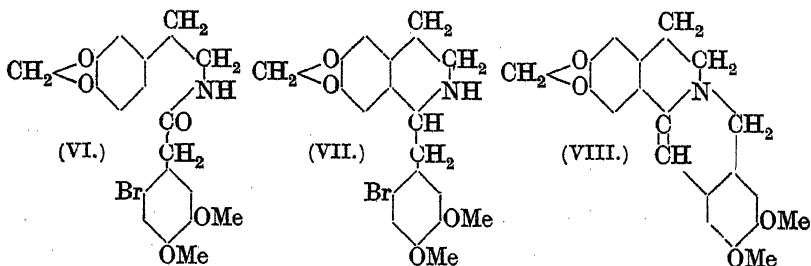
We next prepared 2-formylbromoveratrylnorhydrohydrastinine by heating 6-bromoveratrylnorhydrohydrastinine (VII) with one

molecular proportion of formic acid at 180° and found that this formyl derivative, when treated in the usual manner with phosphorus oxychloride in toluene solution followed by reduction with zinc dust and sulphuric acid, yielded tetrahydro-ψ-berberine (III, *loc. cit.*, p. 1688). This remarkable result shows that, rather than close the *iso*quinoline ring with the aid of the >CH group in the 2'-position of the veratryl nucleus (compare I), the tendency to ring closure in the 6'-position is so great that it will proceed in this direction even when this closure necessitates the elimination of the bromine atom occupying that position.

During the course of this investigation we examined the action of phosphorus oxychloride on the 2'-formyl derivative of veratryl-norhydrohydrastinine (I) and obtained an excellent yield of dihydro-ψ-berberine (VIII) identical with the basic product obtained by the action of sodium hydroxide on ψ-berberinium chloride (*loc. cit.*, p. 1691). In connexion with this and other investigations in the same group, it became very desirable to have some method for rapidly distinguishing between bases of the berberine and ψ-berberine types, and we are indebted to Professor Robinson for the following device which has been found to yield excellent results. Examination of the respective formulæ shows that the structure of tetrahydroberberine (II) differs from that of tetrahydro-ψ-berberine (III) in containing a free position para to a methoxy-group. It was therefore to be expected that tetrahydroberberine would nitrate much more readily than the isomeric base and this has proved to be the case. When tetrahydroberberine is treated with nitric acid in glacial acetic acid solution, 6-*nitrotetrahydroberberine* (V) is obtained and this, on reduction with zinc dust and hydrochloric acid in alcoholic solution, yields an amino-derivative which gives a blue coloration with ferric chloride. Under the same conditions, tetrahydro-ψ-berberine undergoes oxidation and does not yield a nitro-derivative.

<div align="center">EXPERIMENTAL.</div>

6'-*Nitroveratrylnorhydrohydrastinine* (IV).—Veratrylnorhydrohydrastinine (5 g.), dissolved in glacial acetic acid (15 c.c.), was cooled to 0° and mixed with a solution of nitric acid (5 c.c., previously treated with carbamide) in glacial acetic acid (15 c.c.). The mixture was allowed to remain at 0° for a few minutes, poured into water, made slightly alkaline with ammonia, and the cream-coloured precipitate collected, washed, and crystallised from alcohol (Found : C, 64·5; H, 5·3. $C_{19}H_{20}O_6N_2$ requires C, 64·5; H, 5·4%). 6-Nitroveratrylnorhydrohydrastinine separates from alcohol in pale yellow prisms, melts at 149—150°, and slowly becomes green

on exposure to air. This nitro-derivative, dissolved in alcohol containing a little hydrochloric acid and treated with excess of zinc dust, is rapidly reduced; the solution, after filtering, gives a greenish-blue coloration on the addition of a drop of ferric chloride. When the nitro-derivative, dissolved in methyl alcohol, is warmed for a few minutes with formalin, the additive compound is produced and is precipitated as a gum on diluting with water. This was dissolved in concentrated hydrochloric acid and heated under varying conditions on the steam-bath, but in no case could the formation of any nitrotetrahydroberberine be detected.

6-*Nitrotetrahydroberberine* (V).—This substance is readily produced when tetrahydroberberine, dissolved in glacial acetic acid, is mixed with nitric acid; on pouring into water and rendering alkaline with ammonia, the base is precipitated and may be recrystallised from alcohol (Found : N, 7·3. $C_{20}H_{20}O_6N_2$ requires N, 7·3%). This nitro-derivative separates from alcohol or benzene in small, buff-coloured needles, m. p. 185°. It is readily soluble in dilute hydrochloric acid; the amino-derivative produced on the addition of zinc dust gives a greenish-blue coloration with ferric chloride.

6′-*Bromohomoveratroylhomopiperonylamine* (VI).—6-Bromohomoveratric acid was prepared by adding bromine (9 g.) to a solution of homoveratric acid (10 g.) in glacial acetic acid (50 c.c.). After remaining over-night, the crude bromohomoveratric acid was collected; it had the properties described by Pschorr (*loc. cit.*). After gradual crystallisation from water, it sintered at 80°, but rapid crystallisation yielded the acid of m. p. 115°.

The substance (VI) was prepared by heating molecular proportions of the bromohomoveratric acid and homopiperonylamine for one and a half hours at 180°; it crystallised from alcohol in large, rectangular plates, m. p. 159—160° (Found : C, 54·1; H, 4·8. $C_{19}H_{19}O_5NBr$ requires C, 54·1; H, 4·5%). When this substance (5 g.), dissolved in toluene (30 c.c.), was heated with phosphorus oxychloride (12 c.c.) for 1¼ hours, condensation took place readily. The whole was diluted with petroleum (b. p. 40—60°), the solvent decanted from the syrup, the latter dissolved in alcohol, made alkaline with sodium hydroxide, and extracted with benzene. The crude 6′-bromoveratryldihydro*iso*quinoline was extracted from the benzene solution by dilute sulphuric acid and heated on the water-bath for ½ hour with an excess of zinc dust.* The hot solution was filtered, made alkaline with ammonia, extracted with chloroform, the extract dried over potassium carbonate, the solvent removed by distillation, and the residue crystallised from methyl

* When reduction was allowed to proceed for more than ½ hour, considerable quantities of veratrylnorhydrohydrastinine were formed.

alcohol (Found : C, 56·4 ; H, 5·0. $C_{19}H_{20}O_4NBr$ requires C, 56·2 ; H, 4·9%). *6'-Bromoveratrylnorhydrohydrastinine* separates from methyl alcohol in long, colourless needles, m. p. 159—160°. The *hydrochloride* is sparingly soluble in water, from which it crystallises in colourless needles which soften at 250° and melt at 260—262° to a red liquid. The *picrate* was prepared in alcoholic solution and crystallised from alcohol in orange needles, m. p. 174—175°. The 2-hydroxymethyl derivative was obtained by warming the methyl-alcoholic solution of the base with formalin for ½ hour on the water-bath. On diluting the solution with water, an oil separated which rapidly solidified but could not be recrystallised. The *picrate* was readily prepared in methyl-alcoholic solution and separated from methyl alcohol in yellow needles, m. p. 154—155°. The 2-hydroxymethyl derivative, dissolved in concentrated hydrochloric acid, was heated on the steam-bath for varying periods. In some cases it was recovered unchanged and identified by means of the picrate, whilst in other experiments 6'-bromoveratrylnor-hydrohydrastinine was obtained.

2-Formyl-6'-bromoveratrylnorhydrohydrastinine.—A benzene solution of 6'-bromoveratrylnorhydrohydrastinine was mixed with the calculated amount of anhydrous formic acid, when the formate separated as a white, crystalline mass. The benzene was then removed by distillation and the formate heated at 180° for 3 hours. The formyl derivative solidified, on cooling, to a crystalline mass (5 g.), and without further purification was dissolved in toluene (30 c.c.) and heated with phosphorus oxychloride (12 c.c.), when a red oil separated. After ½ hour, excess of petroleum (b. p. 40—60°) was added, the solvent decanted, the residual syrup dissolved in alcohol, mixed with dilute sulphuric acid and reduced with zinc dust during 4 hours. After filtration, the colourless solution was made alkaline with ammonia, extracted with chloroform, dried over potassium carbonate, the chloroform removed by distillation, and the residue crystallised from alcohol. The substance separated in long, colourless needles, melted at 177°, contained no bromine, and was shown to be tetrahydro-ψ-berberine (III) by the mixed melting point method. Identity was confirmed by the preparation of the hydrochloride (m. p. 220°) and the picrate (m. p. 176°).

Action of Phosphorus Oxychloride on 2-Formylveratrylnorhydro-hydrastinine.—Veratrylnorhydrohydrastinine (5 g.) was dissolved in benzene (20 c.c.) and treated with the calculated amount of anhydrous formic acid, when the white crystalline formate separated. The benzene was removed by distillation and the residue heated at 180° for 3 hours, when the decomposition was complete. The crude formyl derivative was dissolved in toluene (30 c.c.) and

heated in the usual manner with phosphorus oxychloride for 1½ hours. The mixture was cooled, shaken with petroleum, the solvent decanted, and the residual syrup dissolved in alcohol, made alkaline with ammonia, diluted with water, and the pale yellow precipitate collected. It crystallised from alcohol or acetone in pale yellow needles, melted sharply at 154—155°,* and proved to be identical with a specimen of dihydroanhydro-ψ-berberine which had been obtained by the action of sodium hydroxide on ψ-berberinium chloride (J., 1924, **125**, 1699). This was confirmed by a mixed melting point and by the preparation of the hydrochloride (m. p. 253—255°, decomp.).

THE DYSON PERRINS LABORATORY,
OXFORD.   [*Received, April 28th*, 1925.]

CXCVII.—*Synthetical Experiments in the* iso*Quinoline Group. Part IV.*

By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

IN the preceding sections of this investigation experiments were described which had for their object the synthesis of certain of the berberine alkaloids, *e.g.*, berberine, palmatine, and corydaline. The present communication deals mainly with an attempt to convert papaveraldine (I) into corydaline (II). The constitution of papaveraldine was first determined analytically by Goldschmiedt (*Monatsh.*, 1886, **7**, 185; 1888, **9**, 8) and the substance has recently been synthesised by Buck, Haworth, and Perkin (J., 1924, **125**, 2176).

(I.)   (II.)   (III.)   (IV.)
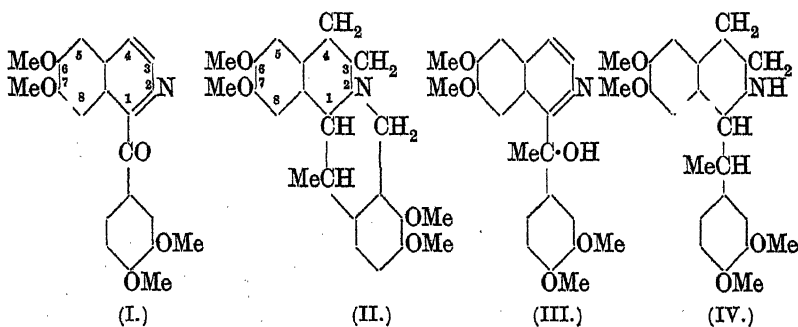
* We should like to take this opportunity of correcting two melting points recorded in our previous communication (J., 1924, **125**, 1686). The melting point of dihydro-ψ-berberine is 154—155° and not 165—167° (p. 1699) and the melting point of *N-o*-nitrobenzoylnorhydrohydrastinine is 160—161° and not 154° (p. 1700).

It seemed reasonable to suppose that papaveraldine, on treatment with magnesium methyl iodide, might yield methylpapaveraldine (III) and that this on reduction would be converted into methyltetrahydropapaverine (IV). Finally, this substance (IV), if it reacted normally with methylal or formaldehyde, should furnish either corydaline (II) or ψ-corydaline (V).
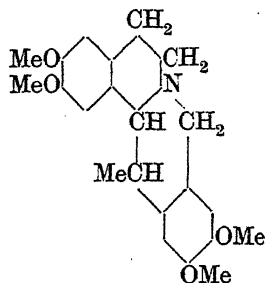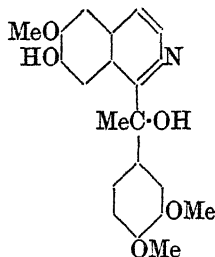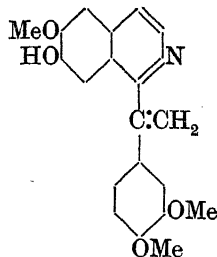
(V.)   (VI.)   (VII.)

When an anisole solution of papaveraldine was allowed to react with one molecular proportion of magnesium methyl iodide, an orange addition product separated which regenerated papaveraldine on decomposition with hydrochloric acid, but when two molecular proportions of magnesium methyl iodide were employed a grey precipitate separated which on decomposition with acids yielded salts of a new base, $C_{20}H_{21}O_5N$ (m. p. 114—116°). During this simple decomposition, there is therefore loss of a methyl group, and as the base is also devoid of ketonic properties, there can be little doubt that it is 7-*demethylomethylpapaverinol* and that its constitution is represented by formula (VI).

Although the elimination of methyl from a methoxy-group usually gives rise to a free hydroxyl group, it apparently does not do so in the case under discussion, for the substance (VI) does not exhibit the ordinary properties of a phenol. It is true that traces dissolve when the substance is shaken with a large excess of dilute alkali and may be recovered on passing carbon dioxide, but all attempts to methylate or acetylate the base have proved unsuccessful. Boiling with excess of acetic anhydride, treatment with phenylcarbimide, or heating with concentrated acids converts the base (VI), by elimination of 1 mol. of water, into a base which is obviously *anhydro-7-demethylomethylpapaverinol* (VII). This substance again behaves as though it does not contain a phenolic hydroxyl group, since it is insoluble in alkalis and cannot be methylated or acetylated.* When

* This curious behaviour has been noticed in a few other cases (compare methylnoroxyberberine : Faltis, *Monatsh*, 1910, **31**, 557; Bland, Perkin, and Robinson, J., 1912, **101**, 262; this vol., p. 744), but the reason why these

7-demethylomethylpapaverinol (VI) or the anhydro-derivative (VII) is reduced with tin and hydrochloric acid, a mixture of substances is obtained from which a base, $C_{20}H_{21}O_4N$ (m. p. 148°), has been isolated and this is probably 7-*demethylomethylpapaverine* (IX). When this substance is reduced with tin and hydrochloric acid, or when the substances (VI) and (VII) are heated with a large excess of the same reducing agent, a base, $C_{20}H_{25}O_4N$ (m. p. 64—65°), is produced which contains three methoxy-groups, yields a *nitrosoamine* (m. p. 124°), and is evidently 7-*demethylomethyl-tetrahydropapaverine* (VIII). This substance is sufficiently basic to combine with carbonic acid from the air, but again does not exhibit phenolic properties.

(VIII.) (IX.) (X.)
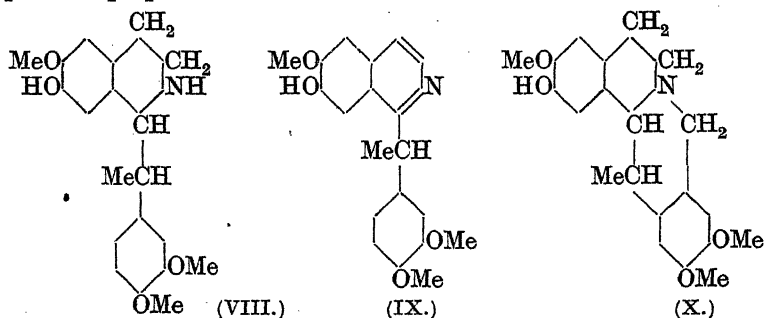
When 7-demethylomethyltetrahydropapaverine (VIII) is warmed with methylal and hydrochloric acid, an interesting new base, $C_{21}H_{25}O_4N$ (m. p. 150—151°), is produced which contains three methoxy-groups and presumably a free hydroxyl group, but attempts to methylate or acetylate the substance were again unsuccessful. The base yields well-characterised salts and the methiodide and methochloride also crystallise well.

We have named this base, which has all the characteristics of tetrahydroberberine, 7-*demethylo-ψ-corydaline* and assign to it the formula (X).

That this substance is related to ψ-corydaline and not to corydaline was proved by making use of the method described in Part III of this series for distinguishing between 3 : 4- and 4 : 5-disubstitution derivatives of veratrole. The base, treated with

substances, produced by demethylation, do not exhibit ordinary phenolic properties is not apparent. It is possible that the grouping MeO·Ç–Ċ(OH)– may become converted by tautomeric change into MeO·ĊH–CO–, and that, in certain positions, this may not be reconvertible into the hydroxy-modification, or the attraction between the phenolic OH-group and the basic nitrogen atom may be so powerful as to render the former inactive.

Experiments with the view of testing these and other possibilities are in progress.

nitric acid in acetic acid solution, clearly did not nitrate, and, on reduction with zinc dust and hydrochloric acid, the colourless solution did not yield the blue coloration with ferric chloride which it should have done had the original base been a derivative of corydaline. The action of the nitric acid was to produce a red substance which was clearly the result of oxidation and had properties resembling those of a substance of the berberinium type. 7-Demethylo-ψ-corydaline (X) is readily oxidised by iodine or mercuric acetate to bright yellow, crystalline salts (p. 1460) which in appearance and properties closely resemble dehydrocorydaline or berberinium salts, but analysis shows that these salts are in reality of the dihydro-7-demethylo-ψ-dehydrocorydaline type (XI. Compare Dobbie and Lauder, J., 1902, 81, 148). This view of their constitution is confirmed by the behaviour of dihydro-7-demethylo-ψ-dehydrocorydalinium chloride with concentrated potassium hydroxide, when it is converted into a mixture of 7-*demethylo-ψ-corydaline* (X) and *ketonor-7-demethylo-ψ-corydaline* (XII) just as berberinium chloride, under the same conditions, yields dihydroberberine and oxyberberine.

(XI.)   (XII.)
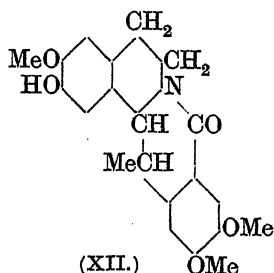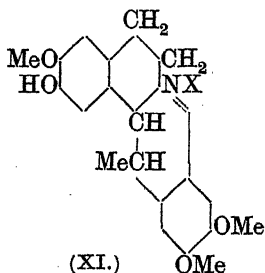
The *methochloride* of 7-demethylo-ψ-corydaline exhibits an interesting behaviour on boiling with potassium hydroxide, when it is converted into an oily base, $C_{22}H_{27}O_4N$, the *hydrochloride* and *picrate* of which are crystalline. There can be little doubt that this base is *anhydro-7-demethylomethyl-ψ-corydaline* and has the constitution represented by (XIII).

(XIII.)   (XIV.)
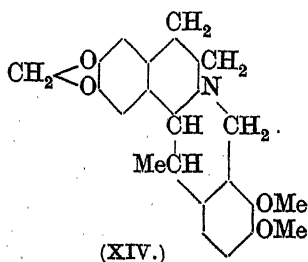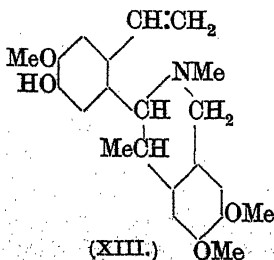
During the course of this investigation we have attempted to synthesise corydaline from the two isomeric modifications of 4-methyltetrahydroberberine (XIV. Freund and Fleischer, *Annalen*, 1915, **409**, 230) by removing the methylenedioxy-group with alcoholic potassium hydroxide (Späth and Lang, *Ber.*, 1921, **54**, 3064) and then methylating the product, but the experiments, which need not be described in detail, were not successful.

EXPERIMENTAL.

The Action of Magnesium Methyl Iodide on Papaveraldine.—(i) An ethereal solution of magnesium methyl iodide prepared from ether (50 c.c.), magnesium (2 g.), and methyl iodide (4·2 g.) was slowly added to a suspension of papaveraldine (10 g.) in anisole (200 c.c.), when an orange precipitate separated. After heating on the steam-bath for an hour, the mixture was decomposed with dilute hydrochloric acid, the ether–anisole layer removed, and the acid extract made alkaline with ammonia. The precipitate was boiled with methyl alcohol, in which papaveraldine is sparingly soluble, and 9 g. of the unchanged base were recovered. (ii) Papaveraldine (30 g.), suspended in anisole (500 c.c.), was mixed with magnesium methyl iodide from magnesium (6 g.), the mixture heated on the steam-bath for an hour, and the grey precipitate collected and decomposed by dilute hydrochloric acid. The acid layer was made alkaline with ammonia, when an oil separated which gradually solidified. A small second crop was obtained by saturating the ammoniacal filtrate with carbon dioxide.

7-Demethylomethylpapaverinol (VI) is somewhat difficult to obtain in a pure condition, but when a small portion of the crude material, dissolved in ether and mixed with petrol (b. p. 40—60°), was left in an open vessel, warts of needles melting at 112—114° gradually separated. On redissolving these in ether and precipitating with petroleum, colourless needles were obtained, m. p. 114—116° [Found : C, 67·3; H, 5·8; MeO, 27·2. $C_{20}H_{21}O_5N$ (containing 3MeO) requires C, 67·6; H, 5·9; MeO, 26·2%]. 7-Demethylomethylpapaverinol dissolves readily in dilute acids to pale yellow solutions, but concentrated acids cause dehydration and formation of the anhydro-derivative (see below). When the substance was warmed with phenylcarbimide for a few minutes, cooled, and mixed with benzene, carbanilide separated and the addition of light petroleum to the filtrate from this caused the separation of colourless needles, m. p. 151°, which were recognised as the anhydro-derivative. Attempts to acetylate 7-demethylomethylpapaverinol by boiling with acetic anhydride and potassium acetate or a few drops of sulphuric acid or camphorsulphonic acid were unsuccessful, the

product in each experiment was the anhydro-derivative. It was also not found possible to methylate the substance by repeated treatment with methyl sulphate and sodium hydroxide; in all such experiments the only substance which could be isolated was the anhydro-derivative.

Anhydro-7-demethylomethylpapaverinol (VII).—This base is readily obtained from 7-demethylomethylpapaverinol by warming for a short time with sulphuric acid (50%) and adding excess of ammonia. It was usually prepared by dissolving the crude product from the Grignard reaction (p. 1457) in concentrated hydrochloric acid, warming on the steam-bath for a short time, and leaving over-night. The hydrochloride of anhydro-7-demethylomethylpapaverinol, which had separated in pale yellow needles, was dissolved in a little water, the base liberated with ammonia, and crystallised from methyl alcohol, from which it separated in small needles, m. p. 151° (Found : C, 71·1; H, 5·7; N, 3·9. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 5·6; N, 4·1%). This anhydro-derivative is. readily soluble in dilute acids to pale yellow solutions; the picrate separates from methyl alcohol in groups of small needles, m. p. 110—112° (decomp.); the *perchlorate* crystallises from aqueous methyl alcohol in pale yellow plates, m. p. 150°.

Attempts to methylate the base, using (i) methyl sulphate and sodium hydroxide, (ii) diazomethane or nitrosomethylurethane and alcoholic potassium hydroxide, were unsuccessful, as were all attempts to acetylate the base by boiling with potassium acetate and acetic anhydride or by other means. The stability of the base is shown by the fact that it may be fused with potassium hydroxide at 180° without decomposition.

7 - *Demethylomethylpapaverine*　(IX).—Anhydro - 7 - demethylo - methylpapaverinol (10 g.), dissolved in alcohol (70 c.c.) and concentrated hydrochloric acid (70 c.c.), was boiled with a large excess of tin for 3 hours. The pale yellow solution was diluted and allowed to remain over-night. The tin double chloride which had separated was washed, dissolved in boiling aqueous alcohol saturated with hydrogen sulphide, the filtrate concentrated, and the base precipitated by ammonia and crystallised from alcohol, from which it separated in colourless needles, m. p. 148° [Found : C, 70·6; H, 6·4; OMe, 28·0. $C_{20}H_{21}O_4N$ (containing 3MeO) requires C, 70·8; H, 6·2; MeO, 27·4%].

7-Demethylomethylpapaverine dissolves readily in dilute mineral acids, but the salts were not obtained crystalline; the picrate, chromate, platinichloride and aurichloride are yellow precipitates which become oily under boiling water. A nitrosoamine could not be obtained by the addition of sodium nitrite to the solution of the base in dilute hydrochloric acid.

Attempts to methylate the base by means of diazomethane or methyl sulphate and sodium hydroxide were unsuccessful, as were also attempts to acetylate the base by boiling with acetic anhydride and potassium acetate.

As the base has almost the same melting point as, and other properties similar to, those of anhydro-7-demethylomethylpapaverinol, a mixed melting-point determination was made; it showed a large depression.

7-Demethylomethyltetrahydropapaverine (VIII).—The reduction either of 7-demethylopapaverinol (VI) or of the anhydro-base (VII) with tin and hydrochloric acid yielded 7-demethylomethyltetrahydropapaverine, presumably owing to the conversion of the former into the anhydro-base under the influence of the concentrated hydrochloric acid employed. The anhydro-base (VII) was boiled in alcoholic solution with tin and hydrochloric acid exactly as described in the preparation of 7-demethylomethylpapaverine (p. 1458). After 12 hours, the solution was almost colourless and, on pouring into water, a tin double salt separated which was decomposed in the usual manner. The base, precipitated as a slime by the addition of sodium hydroxide, was crystallised from aqueous alcohol when long, slender needles, m. p. 64—65°, were obtained (yield about 25%) [Found : C, 69·8; H, 7·1; N, 4·0; MeO, 27·5. $C_{20}H_{25}O_4N$ (containing 3 MeO) requires C, 70·0; H, 7·3; N, 3·9; MeO, 27·1%].

The base dissolves readily in dilute acids and is slowly converted into a carbonate on exposure to air. The *picrate* separates in orange needles from alcohol, darkens at 210°, and melts with decomposition at 225°. The *nitrosoamine* was prepared by dissolving the base in dilute hydrochloric acid and adding sodium nitrite. The sticky precipitate soon hardens and crystallises from methyl alcohol in long, colourless needles, m. p. 124°, which give the Liebermann reaction (Found : N, 7·8. $C_{20}H_{24}O_5N_2$ requires N, 7·5%).

7-Demethylo-ψ-corydaline (X).—In preparing this base, 7-demethylomethylpapaverine (3 g.), dissolved in concentrated hydrochloric acid (15 c.c.) and water (15 c.c.), was heated on the steam-bath under reflux for 1 hour during the gradual addition of methylal (10 c.c.). The clear solution was cooled, diluted with an equal volume of water, made alkaline with sodium hydroxide, and the precipitate collected. This crude base was dissolved in a little methyl alcohol, much ether added, the alcohol removed by washing three times with water, the ethereal solution dried over potassium carbonate, filtered, and allowed to evaporate slowly. Small prisms gradually separated and then the mother-liquor from these deposited an amorphous base (A). After recrystallising from methyl alcohol, the prisms melted at 150—151° [Found : C, 70·6, 70·9; H, 7·1, 7·0;

MeO, 25·2. $C_{21}H_{25}O_4N$ (containing 3MeO) requires C, 71·0; H, 7·0;
MeO, 26·2%].   7-Demethylo-ψ-corydaline is readily soluble in
dilute acids, but does not dissolve in alkalis; if, however, it is
shaken for some time with dilute sodium hydroxide and carbon
dioxide is passed through the filtered solution, a small amount of an
amorphous base (B) separates.   Attempts to obtain an acetyl
derivative by boiling with acetic anhydride and potassium acetate
were unsuccessful, the base being recovered unchanged on the
addition of sodium hydroxide.   It was also not found possible to
methylate the base by treatment with diazomethane or nitroso-
methylurethane and alcoholic potassium hydroxide.   When methyl-
ation was attempted with methyl sulphate and potassium hydroxide
or with methyl iodide and silver hydroxide, quaternary ammonium
salts of the original base were obtained.   The *methiodide* was
prepared by boiling the base with excess of methyl iodide for an
hour, removing the excess by distillation, and dissolving the residue
in boiling water, when, on cooling, the methiodide separated in
colourless, hexagonal prisms, m. p. 250° [Found : C, 53·6; H, 5·8;
MeO, 19·0. $C_{22}H_{28}O_4NI$ (containing 3MeO) requires C, 53·1; H,
5·7; MeO, 18·2%].   The same methiodide was obtained by boiling
the amorphous bases (A) and (B) with methyl iodide.   The metho-
chloride, prepared by digesting the methiodide with water and silver
chloride, is very soluble and was obtained in small, colourless cubes,
m. p. 253° (decomp.), by adding ether to the alcoholic solution.
The hydriodide, prepared by adding potassium iodide to the solution
of the base in dilute hydrochloric acid, crystallises from water in
short, colourless needles, m. p. 242°.

· *The   Dihydro-7-demethylo-ψ-dehydrocorydalinium   Salts.*—When
the solution of 7-demethylo-ψ-corydaline (X) in alcohol containing
potassium acetate is heated to boiling and an alcoholic solution of
iodine gradually added, a sparingly soluble periodide separates in
long, brown needles, m. p. 210°.   The suspension of this in hot water
is decomposed by sulphur dioxide and the yellow solution, on
cooling, deposits small, yellow needles of *dihydro-7-demethylo-
ψ-dehydrocorydalinium iodide*, m. p. 250° (Found : C, 52·6; H, 5·3.
$C_{21}H_{24}O_4NI$ requires C, 52·4; H, 5·0%).   The same iodide was
obtained from nor-ψ-corydaline by oxidising it with a large excess
of mercuric acetate under the conditions described by Perkin
(J., 1918, **113**, 515) in the preparation of the *epi*berberinium salts
from tetrahydro*epi*berberine.   After removal of the mercurous
acetate, the acetic acid solution was diluted with water, saturated
with hydrogen sulphide, and the filtrate concentrated and mixed
with potassium iodide, when, on cooling, the iodide separated in
yellow needles, m. p. 250°.   No depression was observed when this
was mixed with the specimen of the iodide prepared by the iodine

oxidation process described above. The *chloride* was obtained by decomposing the aqueous solution of the iodide with silver chloride, removing the silver salts, and concentrating the filtrate, when the chloride separated in small, yellow needles, m. p. 235° (decomp.) (Found : C, 64·5 ; H, 6·3. $C_{21}H_{24}O_4NCl$ requires C, 64·7 ; H, 6·2%). This chloride dissolves in concentrated sulphuric acid to a yellow solution which becomes brilliant emerald-green on adding a crystal of sodium nitrate ; after a few minutes, the colour changes to bright red.

Keto-7-demethylo-ψ-corydaline (XIII).—This substance is obtained when the chloride (see above) is boiled with a large excess of potassium hydroxide (50%) for 4 hours ; after standing over-night, the mixture of yellow crystals and brown resin is collected, ground, and extracted several times with boiling dilute hydrochloric acid. The insoluble residue is crystallised first from alcohol and then from acetic acid, from which the keto-derivative separates in long, colourless prisms, m. p. 210° (Found : C, 68·1 ; H, 6·3. $C_{21}H_{23}O_5N$ requires C, 68·3 ; H, 6·2%).

Keto-7-demethylo-ψ-corydaline has many properties in common with oxyberberine. It is sparingly soluble in the usual organic solvents except glacial acetic acid and is devoid of basic properties. The solution in concentrated sulphuric acid is yellow and becomes emerald-green and finally deep purple on the addition of a crystal of sodium nitrate. Attempts to methylate this keto-derivative by boiling with methyl sulphate and sodium hydroxide in alcoholic solution and also by means of diazomethane or to acetylate it by boiling with acetic anhydride and sodium acetate for 3 hours were unsuccessful, the substance being recovered in each case.

The acid-soluble portion of the product of the action of potassium hydroxide on 7-demethylo-ψ-corydalinium chloride contained much unchanged chloride. It was heated on the steam-bath, and excess of ammonia added, when an oil was precipitated which rapidly solidified. This substance separated from alcohol in small prisms, melted at 150—151°, and was identified as 7-demethylo-ψ-corydaline (X) by the mixed melting point and by conversion into the meth-iodide, m. p. 250°.

Anhydro-7-demethylomethyl-ψ-corydaline (XIII).—This substance was obtained when a concentrated aqueous solution of the metho-chloride of 7-demethylo-ψ-corydaline (p. 1460) was boiled with a large excess of potassium hydroxide for 6 hours. The oil which had separated was extracted with ether, the ethereal extract dried over potassium carbonate, and the solvent evaporated, when a gum remained which hardened to a resin, but could not be obtained crystalline.

The base was dissolved in dilute hydrochloric acid, the solution

evaporated to dryness under diminished pressure, and the residue dissolved in methyl alcohol. On the addition of ether, the hydrochloride separated in small needles, m. p. 228° (decomp.) (Found : C, 65·0; H, 7·1. $C_{22}H_{28}O_4NCl$ requires C, 65·1; H, 6·9%). The hydriodide, obtained by the addition of potassium iodide to the aqueous solution of the hydrochloride, separates from water in small needles, m. p. 232°. The *picrate*, prepared by the addition of picric acid to the alcoholic solution of the base, crystallises from alcohol in long, yellow needles which froth to a turbid liquid at 130°, melt completely at 165°, and evidently contain alcohol of crystallisation (Found : C, 55·7; H, 6·2; N, 8·3. $C_{28}H_{30}O_{11}N_4,2C_2H_6O$ requires C, 55·7; H, 6·1; N, 8·1%).

CXCVIII.—*Synthesis of* 2:3:10:11-*Bismethylenedioxy-protoberberine and* 6:7:3':4'-*Bismethylenedioxy-protopapaverine.**

By JOHANNES SYBRANDT BUCK, WILLIAM HENRY PERKIN, jun., and THOMAS STEVENS STEVENS.

DURING the course of experiments which led to the synthesis of ψ-*epi*berberine (Buck and Perkin, J., 1924, **125**, 1675), a parallel

* The nomenclature of the substances obtained during the course of this investigation, and of other investigations which are in progress, has caused considerable difficulty, and it is suggested, with the concurrence of the Editor, that the parent substances of berberine and papaverine,
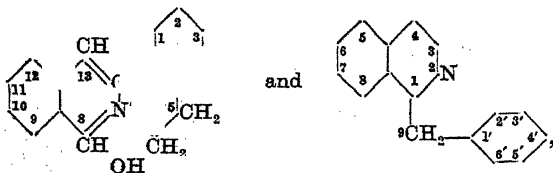
should be named protoberberine and protopapaverine, respectively.

investigation was undertaken with a view to prepare substances bearing the same relation to protopine as *epi*berberine and its derivatives bear to cryptopine. It was, of course, expected at that time that the products obtained would be related to protopine (I), and not to ψ-protopine (II), but, although we have as yet no direct proof of this, there can be little doubt that these substances are of the type (II).

(I.)   (II.)
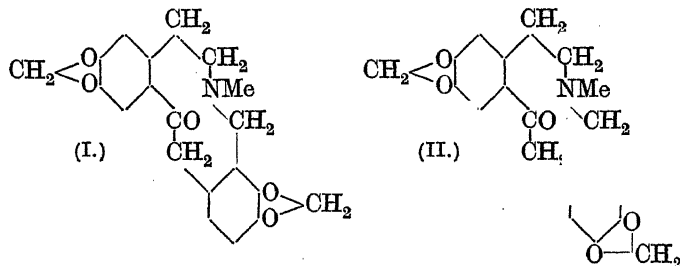
The synthesis was carried out on lines similar to those which had led to the preparation of ψ-*epi*berberine (Buck and Perkin, *loc. cit.*) and of ψ-berberine (Haworth, Perkin, and Rankin, J., 1924, **125**, 1686). Homopiperonoylhomopiperonylamine (III), which had previously been described by Decker (*Annalen*, 1913, **395**, 282), was prepared by heating together homopiperonylamine and homopiperonylic acid, and transformed, by boiling with phosphorus oxychloride in toluene solution, into 6 : 7 : 3′ : 4′-*bismethylene-dioxy*-3 : 4-*dihydroprotopapaverine* (IV), a crystalline substance (m. p. 92—96°) which rapidly oxidises in the air to the corresponding ketone. The substance (IV) is reduced smoothly by means of zinc dust and dilute sulphuric acid to 6 : 7 : 3′ : 4′-*bis-methylenedioxy*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (V).

(III.)   (IV.)   (V.)
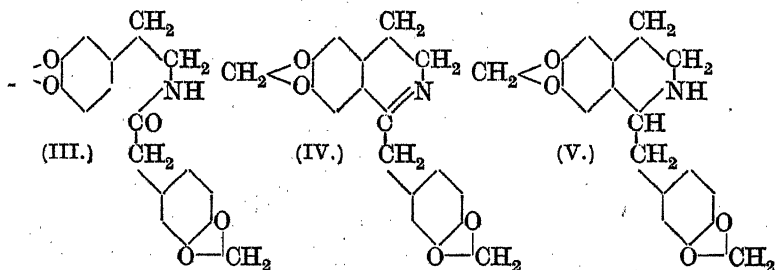
By successive treatment with formaldehyde and hydrochloric acid, the tetrahydro*iso*quinoline is converted, no doubt through its *N*-hydroxymethyl derivative, into the hydrochloride of 2 : 3 : 10 11-*bismethylenedioxytetrahydroprotoberberine* (VI). This base resembles its analogues, tetrahydro-ψ-berberine (m. p. 177°)

and tetrahydro-ψ-*epi*berberine (m. p. 160—161°) in most of its properties, but differs noticeably in its high melting point (214°) and its comparative insolubility in alcohol. It is readily oxidised by iodine in presence of sodium acetate, with the formation of 2 : 3 : 10 : 11-*bismethylenedioxyprotoberberinium iodide* (VII), which is converted into the corresponding *chloride* by digestion with water and silver chloride. This chloride crystallises from hot water with two molecules of water of crystallisation, one of which is lost at 110°, and the other on recrystallisation from acetic anhydride.

CH₂ $<$ O O ... (VI.) ... CH₂ ... N ... CH ... CH₂ ... O—CH₂

CH₂ $<$ O O ... (VII.) ... CH₂ ... N—I ... CH ... O ... CH₂
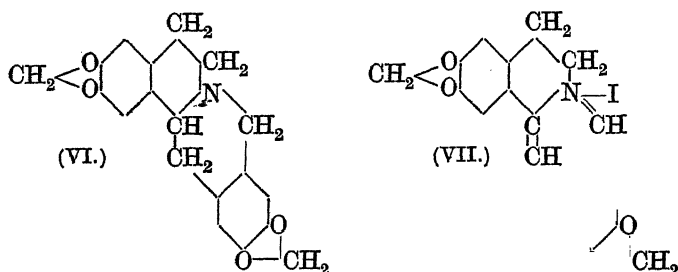
On treatment with hot sodium hydroxide solution, this quaternary chloride undergoes a transformation in the same manner as berberinium chloride, yielding a mixture of 2 : 3 : 10 : 11-*bismethylenedioxyoxyprotoberberine* (VIII), analogous to oxyberberine, and 2 : 3 : 10 : 11-*bismethylenedioxydihydroprotoberberine* (IX), corresponding to dihydroberberine.

(VIII.) ... CH₂ $<$ O O ... CH₂ ... N ... CO ... CH ... O CH₂

(IX.) ... CH₂ $<$ O O ... CH₂ ... N ... CH₂ ... CH ... O—CH₂
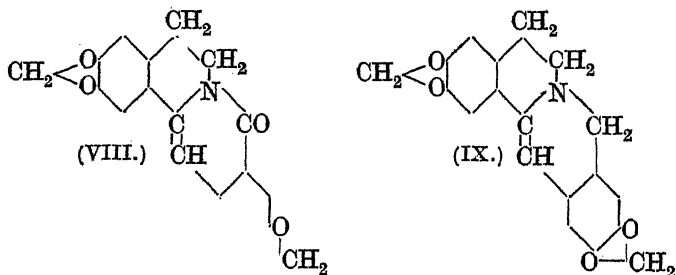
It has been shown in a previous communication (Buck, Haworth, and Perkin, J., 1924, **125**, 2176) that several derivatives of 1-benzyl-3 : 4-dihydro*iso*quinoline are readily converted by atmospheric oxidation into the corresponding derivatives of benzoyldihydro*iso*quinoline, and the substance (IV) behaves in perfectly analogous fashion. On exposure of its alcoholic solution to the air for a few days, it is oxidised to 6 : 7 : 3′ : 4′-*bismethylenedioxy-9-keto-3 : 4-dihydroprotopapaverine* (X), which crystallises in long needles melting at 136°, and, like the analogous substances previously examined, forms

yellow salts and gives an emerald-green coloration on boiling with acetic anhydride. It is worthy of note that Decker, Kropp, Hoyer, and Becker (*Annalen*, 1913, **395**, 299) treated homopiperonoyl-homopiperonylamine with phosphorus oxychloride and isolated a picrate which gave on decomposition a substance melting at 136—137° and forming yellow salts. It would seem highly probable that the compound obtained by these authors, to which they attributed the structure (IV), is really identical with (X).
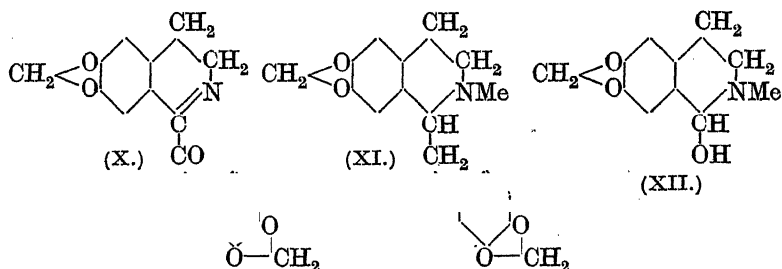
Decker briefly states in another communication that by methylation and reduction of this product he obtained a tetrahydro*iso*quinoline derivative (XI), which gave on oxidation piperonal and hydrastinine (XII), a result which proves that, as was to be expected, the action of phosphorus oxychloride on homopiperonoylhomo-piperonylamine takes the course indicated and does not lead to the isomeric 7 : 8 : 3' : 4'-bismethylenedioxy-1 : 2 : 3 : 4-tetrahydro-protopapaverine (XIII).
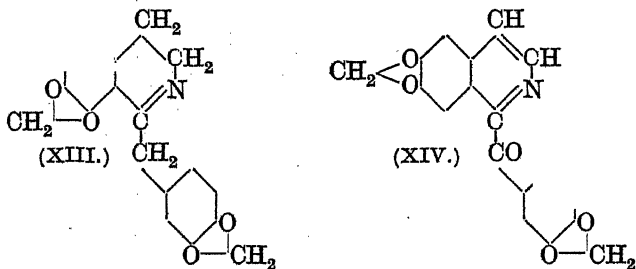
When the ketone (X) is boiled with methyl-alcoholic potassium hydroxide solution, it is rapidly oxidised with production of 6 : 7 : 3' : 4'-*bismethylenedioxy-9-ketoprotopapaverine* (XIV), a weakly basic substance, which, like papaveraldine, forms yellow salts. Stuchlik (*Monatsh.*, 1900, **21**, 814), without giving any experimental details, states that Goldschmiedt obtained papaverine by reducing papaveraldine with zinc dust and acetic anhydride. With the ultimate object of applying the method to the substance (XIV), we

made repeated attempts, under various conditions, to carry out this reaction, but it was not found possible to obtain a satisfactory yield of papaverine, and, owing to the inaccessibility of the compound (XIV), it was necessary to devise a more suitable process. Since the tetrahydro*iso*quinoline derivative (V) is comparatively easily obtainable, an attempt was made to oxidise the analogous tetrahydropapaverine by means of iodine, but the main product of the reaction was 6 : 7 : 3′ : 4′-*tetramethoxy-9-keto-3 : 4-dihydroprotopapaverine* (XV).
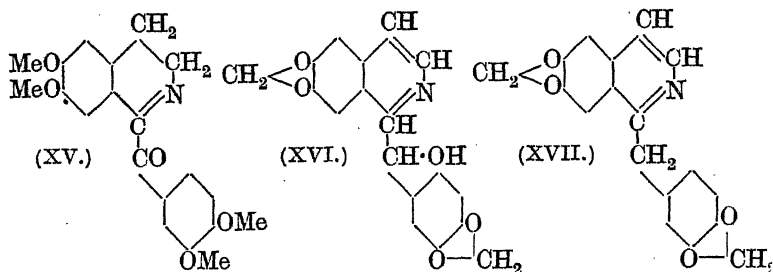
Ultimately it was found that papaverinol could be readily converted into papaverine by the action of an acetic acid solution of hydrogen bromide, followed by reduction with zinc dust. The substance (XIV) was then reduced with zinc dust and acetic acid to give the papaverinol analogue, 6 : 7 : 3′ : 4′-*bismethylenedioxy-9-hydroxyprotopapaverine* (XVI), which was then further reduced in the manner just described, and yielded the required 6 : 7 : 3′ : 4′-bismethylenedioxyprotopapaverine (XVII).

EXPERIMENTAL.

Homopiperonoylhomopiperonylamine (III).—The homopiperonylic acid and homopiperonylamine used in the preparation of this substance were obtained as described, respectively, by Buck and Perkin (*loc. cit.*) and by Haworth, Perkin, and Rankin (*loc. cit.*). The procedure employed by Decker (*loc. cit.*) was modified in that the materials were heated at 190°, at which temperature the reaction is completed in 2 hours.

6 : 7 : 3′ : 4′ - *Bismethylenedioxy* - 3 : 4 - *dihydroprotopapaverine* (IV).—Homopiperonoylhomopiperonylamine (45 g.), toluene (225 c.c.), and phosphorus oxychloride (90 c.c.) are boiled under reflux for 15 minutes. On cooling, the mixture is diluted with light petroleum, and after a few minutes the supernatant liquid is decanted from the light brown gum. After washing thoroughly with ether, the gum is dissolved in aqueous alcohol, and, on addition of ether, the solution deposits a cream-coloured phosphate, which is

recrystallised from alcohol–ether. The salt is dissolved in dilute alcohol, treated with excess of potassium hydroxide solution, and water cautiously added, when the free base separates in nearly colourless needles, m. p. 92—96° (Found : C, 69·4; H, 4·8; N, 4·2. $C_{18}H_{15}O_4N$ requires C, 69·9; H, 4·9; N, 4·5%). The substance could not be further purified, as it oxidised quickly in the air. It is readily soluble in alcohol, and dissolves in dilute acids with a pale yellow colour. The *picrate* separates from alcohol–acetic acid in pale yellow needles, m. p. 220° (blackening and effervescence) (Found : C, 53·9; H, 3·6. $C_{18}H_{15}O_4N,C_6H_3O_7N_3$ requires C, 53·5; H, 3·4%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-1 : 2 : 3 : 4-*tetrahydroprotopapaverine* (V).—In the preparation of this substance it is unnecessary to isolate the last-mentioned product. The brown gum remaining after decantation of the toluene and light petroleum is dissolved in alcohol, treated with excess of sodium hydroxide solution, largely diluted with water, and extracted with benzene. The benzene extract is shaken with dilute sulphuric acid (a litre of 10—15%), and the acid layer reduced on the steam-bath with a considerable excess of zinc powder. During the reaction, the product separates as sulphate, and is redissolved by boiling the liquid, which is then filtered, rendered strongly alkaline with sodium hydroxide solution, and extracted with ether. On standing, the ethereal extract deposits the tetrahydro-derivative in large crystals, m. p. 84—85°, the yield being 70—75% of that theoretically obtainable from the original homopiperonoylhomopiperonylamine (Found : C, 69·5; N, 5·6; N, 4·1. $C_{18}H_{17}O_4N$ requires C, 69·4; H, 5·5; N, 4·5%). The substance (V) is readily soluble in the usual organic solvents, and tends to separate from them as an oil. It dissolves in dilute acids to form colourless, rather sparingly soluble salts, and in concentrated sulphuric acid to give a dark yellow solution, which turns reddish-brown on addition of a crystal of potassium nitrate. From solutions of the hydrochloride, potassium iodide precipitates the *hydriodide* as a gum, which solidifies on scratching, and crystallises from much hot-water in groups of small, white needles, m. p. 250—254°. The *picrate* crystallises from alcohol–acetic acid in minute, bright orange needles, which soften at 190° and melt with decomposition at 210° (Found : C, 53·3; H, 4·1. $C_{18}H_{17}O_4N,C_6H_3O_7N_3$ requires C, 53·3; H, 3·7%).

2 : 3 : 10 : 11-*Bismethylenedioxytetrahydroprotoberberine* (VI).—The last-mentioned base (6 g.) is dissolved in boiling methyl alcohol (30 c.c.), and sodium bicarbonate (3 g.) and formalin (10 c.c. of 40%) are successively added. After warming for a short time, the liquid is diluted, and the white gum which separates completely

is precipitated by addition of sodium chloride, washed free from formaldehyde, and dissolved in hot concentrated hydrochloric acid (40 c.c.). The white hydrochloride which crystallises on cooling is collected, dissolved in hot aqueous alcohol, and treated with ammonia, when the base separates in small, white needles. A further quantity may be obtained from the acid mother-liquors, making a total yield of 80% of theory. In some experiments, the hydrochloride was obtained in a highly insoluble form, which, however, gave the same base on decomposition. Bismethylenedioxytetrahydroprotoberberine crystallises from much alcohol in small, white needles, m. p. 214° (Found : C, 70·7; H, 5·4; N, 4·1. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3; N, 4·3%). This substance, which slowly turns brown in the air, is rather sparingly soluble in alcohol or acetone, but more readily soluble in benzene and especially in chloroform. It dissolves readily in cold acetic acid and slowly separates if the solution be diluted with water or alcohol. With dilute mineral acids it forms stable, rather sparingly soluble salts; when concentrated sulphuric acid is added to a solution of the base in acetic acid, a yellow solution is obtained, which turns red on addition of a crystal of potassium nitrate.

2 : 3 : 10 : 11-*Bismethylenedioxyprotoberberinium Iodide* (VII).— The tetrahydro-compound (VI) (25 g.) and sodium acetate (80 g.) are dissolved in hot alcohol (700 c.c.), with the addition of sufficient acetic acid to bring about solution, and iodine (40 g.), dissolved in alcohol, is gradually added. The iodine is rapidly absorbed, and the quaternary iodide soon separates as a yellow powder, which is collected on cooling : the yield is 30 g. This highly insoluble salt crystallises in small, bright yellow rods, which have an intensely bitter taste and decompose without melting above 300°. The corresponding *chloride* is obtained by digesting the iodide on the steam-bath with a slight excess of silver chloride and 40 parts of water for 2 hours and filtering hot from the silver salts; when the chloride separates on cooling in bright yellow needles which may be recrystallised from dilute hydrochloric acid. The air-dried salt has the composition $C_{19}H_{14}O_4NCl,2H_2O$, and loses $1H_2O$ at 110° (Found : loss at 110°, 4·2; Cl, 9·3. $C_{19}H_{14}O_4NCl,2H_2O$ requires loss, 4·6; Cl, 9·1%. The salt dried at 110° gave C, 61·1; H, 4·4. $C_{19}H_{14}O_4NCl,H_2O$ requires C, 61·0; H, 4·3%). When the substance is recrystallised from acetic anhydride, in which it is moderately soluble, it separates in the anhydrous condition in pale yellow needles, which decompose above 300° and dissolve in concentrated sulphuric acid to a pale yellow solution (Found : C, 64·0; H, 4·0. $C_{19}H_{14}O_4NCl$ requires C, 64·1; H, 3·9%). The *picrate* is obtained by adding excess of aqueous picric acid to a hot solution of the

chloride, and recrystallising the precipitate from a large quantity of acetic acid, from which it separates in bright orange-yellow needles, which darken above 260° and explode at 310° (Found : C, 54·7; H, 2·9. $C_{19}H_{14}O_4N,C_6H_2O_7N_3$ requires C, 54·7; H, 3·1%). It is noteworthy that this salt separates in the anhydrous condition, whilst the analogous berberinium, ψ-berberinium, and ψ-*epi*berberinium picrates contain an additional molecule of water.

2 : 3 : 10 : 11 - *Bismethylenedioxyoxyprotoberberine* (VIII) *and* 2 : 3 : 10 : 11 - *Bismethylenedioxydihydroprotoberberine* (IX). — The quaternary chloride (5 g.) is dissolved in boiling water (150 c.c.), added to potassium hydroxide solution (100 c.c. of 40%), and the mixture heated at 100°. The brown gum, which separates, soon solidifies, and is then ground up and the heating continued for 3 hours. After cooling, the solid is collected, washed with water, finely powdered, and extracted three times with hot dilute hydrochloric acid (80 c.c. of $2N$ in all). The residue is dissolved in hot acetic acid, and *bismethylenedioxyoxyprotoberberine* separates on cooling in fine, pale yellow needles, which are very insoluble in most organic solvents except acetic acid, and melt above 270° : the yield is about 2 g. (Found : C, 68·2; H, 3·9; N, 4·3. $C_{19}H_{13}O_5N$ requires C, 68·1; H, 3·9; N, 4·2%). The substance is insoluble in dilute mineral acids, and, unlike oxyberberine and oxy*epi*berberine, separates from acetic acid in the free state, and not as acetate. Its solution in 50% sulphuric acid turns brownish-violet on addition of a drop of concentrated nitric acid.

When the united hydrochloric acid extracts, obtained as described above, are cooled to 0°, they deposit yellow crystals, which are then dissolved in hot water and treated with excess of ammonia; and the brown gum, which separates and soon solidifies, is collected. This material is extracted with much acetone and the extract concentrated, when some brown solid separates on standing. The filtrate from this solid is then warmed, and, after a little water has been added, deposits, on cooling, bright yellow leaflets of *bis*-*methylenedioxydihydroprotoberberine* (0·7 g.) (Found : C, 71·2; H, 5·0; N, 4·6. $C_{19}H_{15}O_4N$ requires C, 71·0; H, 4·7; N, 4·4%). The base melts at 161—164°, and dissolves readily in acetone to a bright yellow solution with a green fluorescence. With strong sulphuric acid, it forms a dark yellow solution which turns reddish-brown on addition of a crystal of potassium nitrate. The *picrate* separates from acetic acid, in which it is sparingly soluble, in small golden-brown prisms, which gradually darken and decompose above 240° (Found : C, 54·5; H, 3·3. $C_{19}H_{15}O_4N,C_6H_3O_7N_3$ requires C, 54·5; H, 3·2%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-9-*keto*-3 : 4-*dihydroprotopapaverine*
(X).—The substance (IV) is dissolved in ether–methyl alcohol
and exposed to the air for 10 days, the solvents being renewed at
intervals. The product is dissolved in methyl alcohol, with the
addition of a little hydrochloric acid, and rendered alkaline with
ammonia, when crystals are deposited, along with tarry matter,
which renders their purification rather tedious. After recrystal-
lising several times from methyl alcohol, the base forms long,
colourless needles, m. p. 136° (Found : C, 67·3; H, 4·5; N, 4·1.
$C_{18}H_{13}O_5N$ requires C, 66·9; H, 4·0; N, 4·3%). The substance
is readily soluble in the usual solvents, and dissolves in dilute acids
to give bright yellow salts, which are mostly easily soluble. Its
solution in acetic anhydride turns emerald-green on boiling. The
hydriodide is precipitated when solid potassium iodide is added to
a solution of the hydrochloride, and separates from alcohol–ether
in minute, yellow prisms, m. p. 216—219° (decomp.), which are
fairly soluble in hot alcohol. The *picrate* crystallises from alcohol–
acetic acid in minute, orange-yellow plates, m. p. 202° (decomp.;
softening above 180°) (Found : C, 52·6; H, 3·3. $C_{18}H_{13}O_5N,C_6H_3O_7N_3$
requires C, 52·2; H, 2·9%). The *oxime* is obtained by heating a
mixture of the base (0·5 g.), pyridine (4 c.c.), alcohol (1 c.c.), and
hydroxylamine hydrochloride (0·15 g.) on the water-bath for 2 hours.
On diluting the mixture with water and saturating with carbon
dioxide, a white solid is precipitated, which is recrystallised from
methyl alcohol. This oxime forms a white powder, m. p. 235°
(decomp.), which is sparingly soluble in the usual organic solvents
and dissolves in concentrated sulphuric acid with an orange colour
(Found : C, 64·0; H, 3·9. $C_{18}H_{14}O_5N_2$ requires C, 63·9; H, 4·1%).

6 : 7 : 3′ : 4′-*Bismethylenedioxy*-9-*ketoprotopapaverine* (XIV).—The
base (X) (3 g.) is heated on the steam-bath for $\frac{1}{2}$ hour with 10%
methyl-alcoholic potassium hydroxide (30 c.c.). After cooling, the
solid is collected and recrystallised from alcohol, from which it
separates in fine, colourless needles, m. p. 186° (yield 50%) (Found :
C, 61·2; H, 3·4; N, 4·5. $C_{18}H_{11}O_5N$ requires C, 67·3; H, 3·4;
N, 4·4%). The substance is moderately soluble in hot alcohol, and
readily soluble in acetic acid, from solutions in which it separates
at once on dilution with water. It dissolves readily in dilute
mineral acids, forming yellow salts, and in concentrated sulphuric
acid to a deep orange-red solution. On boiling with acetic anhydr-
ide, a pale green liquid is produced. When potassium iodide is
added to a solution of the base in dilute hydrochloric acid, the
sparingly soluble *hydriodide* separates in minute, yellow prisms,
which are completely hydrolysed by hot water, darken above 210°,
and melt with decomposition at about 230°. The *picrate* is pre-

pared in alcoholic solution, and crystallises from alcohol–acetic acid in well-defined, short, yellow prisms, m. p. 240° (decomp.) (Found: C, 52·6; H, 2·6. $C_{18}H_{11}O_5N,C_6H_3O_7N_3$ requirees C, 52·4; H, 2·5%). The *oxime* is obtained by heating the base (0·5 g.) with hydroxylamine hydrochloride (1·5 g.) and potassium acetate (2 g.) in alcoholic solution on the steam-bath for 8 hours. The liquid is then filtered, concentrated, and slightly diluted with water, when the oxime separates on cooling as a white powder, which crystallises from alcohol in minute, transparent laminæ, melting with blackening and effervescence at about 275° (Found: C, 63·9; H, 3·9; N, 8·2. $C_{18}H_{12}O_5N_2$ requires C, 64·3; H, 3·6; N, 8·3%). It is rather sparingly soluble in the ordinary solvents.

6 : 7 : 3′ : 4′-*Bismethylenedioxy* - 9 - *hydroxyprotopapaverine* (XVI. Compare Stuchlik, *Monatsh.*, 1900, **21**, 814).—The ketone (XIV) (1 g.) is dissolved in acetic acid (10 c.c.), and reduced on the steam-bath with a moderate excess of zinc powder, added during 3 hours. The hot liquid is filtered, the residue washed with hot water, and the filtrate diluted to 100 c.c.; no appreciable quantity of unaltered material separates on standing. The zinc is precipitated by means of hydrogen sulphide, the filtrate concentrated on the steam-bath, nearly neutralised with solid sodium carbonate, rendered strongly alkaline with ammonia, and extracted with chloroform. After removing the chloroform, the residue is recrystallised from benzene, from which it separates in short, colourless prisms, m. p. 169—170° (Found: C, 66·6; H, 4·3. $C_{18}H_{13}O_5N$ requires C, 66·9; N, 4·0%). The base is moderately soluble in alcohol or benzene, very sparingly soluble in light petroleum, and dissolves in concentrated sulphuric acid to give a deep bluish-violet solution, which turns yellowish-brown on addition of a crystal of potassium nitrate. Its salts, like those of papaverinol, are fairly soluble in water and do not crystallise readily.

6 : 7 : 3′ : 4′-*Bismethylenedioxyprotopapaverine* (XVII).—The substance (XVI) is dissolved in 10—20 parts of acetic acid, saturated with hydrogen bromide, and allowed to remain for 12 hours The solution is then warmed to 25°, stirred mechanically, and reduced during 1—1½ hours with a considerable excess of zinc powder, the reaction being completed by warming at 50°. The liquid is then diluted, rendered strongly alkaline with ammonia, and extracted with chloroform. After evaporating the chloroform, the base is recrystallised from benzene, and separates in small balls of needles, m. p. 170—172°, which give an intense bluish-violet coloration with concentrated sulphuric acid (Found: C, 70·3; H, 4·6. $C_{18}H_{13}O_4N$ requires C, 70·4; H, 4·2%). The *picrate* separates slowly from alcohol in minute, pale yellow prisms, m. p. 199—202° (decomp.).

The conversion of papaverinol into papaverine is readily carried out by the method just described : during the reduction, a highly insoluble double zinc bromide separates, which is collected, dissolved in much boiling water, and treated with excess of ammonia, and the base then isolated in the usual manner.

Oxidation of Tetrahydropapaverine.—This base, prepared as described by Pyman (J., 1909, **95**, 1614), and an excess of sodium acetate were dissolved in alcohol on the steam-bath, and iodine (slightly more than 4 atoms) was added in alcoholic solution during 3 hours. The iodine was at first rapidly absorbed, and the solution became dark brown. After being treated with sulphur dioxide and most of the alcohol removed by evaporation, the liquid was diluted with water, rendered alkaline with ammonia, and extracted with chloroform. The chloroform extract was washed with dilute hydrochloric acid, which removed very little material, and on concentrating the chloroform solution, yellow crystals of the hydrochloride of a base melting at 190—191° were obtained. The substance gave a green solution on boiling with acetic anhydride, and no depression in melting point was observed on mixing with a specimen of 6 : 7 : 3' : 4'-tetramethoxy-9-keto-3 : 4-dihydroprotopapaverine (XV), prepared by Buck, Haworth, and Perkin (*loc. cit.*) by the atmospheric oxidation of the corresponding benzyl-dihydro*iso*quinoline. Concentration of the chloroform mother-liquors from this hydrochloride gave small quantities of two scarcely basic substances, melting at 300° and 163—167°, which were not farther examined.

CXCIX.—*Alcohols of the Hydroaromatic and Terpene Series. Part IV. α- and β-Fenchyl Alcohols and some Esters derived therefrom.*

By JOSEPH KENYON and HAROLD EDWARD MEAD PRISTON.

WHEN *d*-fenchone is reduced, a mixture of two isomeric fenchyl alcohols is produced. Each of these alcohols when isolated in an optically pure condition exhibits lævorotation and on oxidation

regenerates a ketone which is identical with the d-fenchone from which it was obtained. These fenchyl alcohols must therefore be stereoisomerides; a view which is in harmony with stereochemical considerations of the fenchone molecule and also with the general behaviour of optically active cyclic ketones on reduction. For example, it has been shown in Part II * of this series that l-menthone on reduction gives a mixture of l-menthol and d-neomenthol and in Part I that d-camphor on reduction gives a mixture of d-borneol and l-isoborneol, and further, using the same method, Tschugaev (*Ber.*, 1912, **45**, 1293) showed that tanacetone on reduction yields two tanacetyl alcohols of opposite, but unequal, rotatory powers.

Although these two fenchyl alcohols possess the same sign of rotation and thus differ from the other pairs mentioned above, yet in some respects they show rotatory effects of an opposite character, as will be seen from the following table of the rotatory powers of α- and β-fenchyl alcohols and some of their esters.

Specific Rotatory Power, $[\alpha]_{5461}^{20°}$.

			Homogeneous.	Ethyl alcohol.	Carbon disulphide.
α-Fenchyl alcohol		....	$-15 \cdot 04°$	$-15 \cdot 37°$	$-6 \cdot 70°$
β-	,,	,, ...	$-27 \cdot 97$	$-26 \cdot 23$	$-38 \cdot 27$
α-	,,	formate	$-80 \cdot 67$	$-86 \cdot 50$	$-72 \cdot 51$
β-	,,	,, ...	$-12 \cdot 88$	$-11 \cdot 74$	$-15 \cdot 79$
α-	,,	acetate	$-75 \cdot 73$	—	—
β-	,,	,, ...	$-16 \cdot 90$	—	—
α-	,,	p-nitrobenzoate	—	—	$-23 \cdot 2$
β-	,,	,, ...	—	—	$+13 \cdot 5$
α-	,,	hydrogen phthalate	—	$+27 \cdot 0$	—
β-	,,	,, ,, ...	—	$+13 \cdot 3$	—

A further example of this behaviour is found in the temperature–rotation curves of the α- and the β-alcohols : that for the β-alcohol reaches a maximum and then falls slowly, whilst that for the α-alcohol falls to a minimum and then rises.

In each case, conversion of α-fenchyl alcohol into a neutral ester has given a compound which possesses a considerably higher lævorotatory power than the alcohol from which it was derived, whilst the conversion of β-fenchyl alcohol into neutral esters yields compounds which possess considerably lower lævorotatory powers than the parent alcohol—in one case, that of the p-nitrobenzoate, the sign of rotation has become positive. There is, however, an anomaly in the case of the hydrogen phthalic esters, which both possess dextrorotatory powers. The effect of solvents on rotatory power is in opposite directions in the cases of α- and β-fenchyl alcohols and α- and β-fenchyl formates.

* Part I, J., 1907, **91**, 1979 ; Part II, J., 1912, **101**, 109.

α-*Fenchyl alcohol* is readily separated from the mixture of alcohols obtained by the reduction of *d*-fenchone by the following method. The mixture of hydrogen phthalates obtained by heating the alcohols with phthalic anhydride is crystallised from acetic acid until a product of constant rotatory power is obtained : this is pure α-fenchyl hydrogen phthalate. The more soluble fractions of the hydrogen phthalates are hydrolysed, and the resulting fenchyl alcohol is converted into the *p*-nitrobenzoate. This ester is crystallised from ethyl alcohol until constancy of rotation is reached : this yields as the less soluble fraction pure β-fenchyl *p*-nitrobenzoate. Hydrolysis of the hydrogen phthalate of constant rotatory power gives pure α-fenchyl alcohol, whilst the *p*-nitrobenzoate yields on hydrolysis pure β-fenchyl alcohol. Details of the various operations involved are recorded in the experimental part. The other esters were prepared by the usual methods.

In view of the general similarity in structure of the camphor and fenchone molecules it was thought that an examination of some simple esters of borneol and of *iso*borneol would throw light on the relations between α- and β-fenchyl alcohols. A number of these have been prepared and their rotatory powers determined both in the homogeneous condition over a wide range of temperature and in solution. This is the first recorded case of the examination of two series of esters derived from *cis*- and *trans*-isomeric alcohols. Under the experimental conditions employed, the esters of both series possess simple rotatory dispersion.

The curve connecting the specific rotatory powers of the bornyl esters is similar in character to that for the corresponding α-fenchyl esters, whilst the curve for the *iso*bornyl esters is similar to that for the corresponding β-fenchyl esters. The temperature–rotation curves of the bornyl esters and the *iso*bornyl esters are similar to those of the α- and the β-fenchyl esters—the rotatory powers in all cases decreasing regularly with rise of temperature.

In general, therefore, the bornyl and *iso*bornyl esters bear much the same relation to each other as do the α- and β-fenchyl esters.

The Relation between the Specific Rotatory Powers of Members of Homologous Series of Esters and the Length of the Acyl Group.

A consideration of the values of the specific rotatory powers of the members of the four homologous series of esters now described affords a good illustration of the complexity of the problem involved in attempting to discover the relations which may exist between chemical constitution and optical activity and of the difficulty of drawing deductions of a general character. When their specific rotatory powers, $[\alpha]_{5461}$, are plotted against the number of carbon

atoms in the growing acyl chain, four different types of curves are obtained which may be briefly described as follows :—

(1) *Bornyl Esters.*—The five esters of this series lie on a smooth curve which falls steadily and fairly rapidly from the first member to the last.

(2) iso-*Bornyl Esters.*—The first member has a relatively very low value : there is then a big jump to the second member, after which the values for the remaining three members fall steadily but slowly.

(3) β-*Fenchyl Esters.*—The curve is similar in character to that given by the *iso*bornyl esters except that the relatively low value for the first member of the series is not so pronounced and the values from the second member onwards fall much more rapidly.

(4) α-*Fenchyl Esters.*—These lie on a smooth curve which falls steadily from the first member to the last. There are, however, three notable exceptions—a pronounced exaltation is shown by the propionate and a second pronounced exaltation by the *n*-heptoate and the *n*-octoate. In these three cases the asymmetric carbon atoms (which form part of a ring system) together with the acyclic acyl groups form chains which contain respectively five, nine, and ten atoms, thus :

$$>CH-O-\overset{\overset{O}{\|}}{C}-CH_2-CH_3.$$
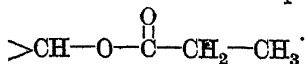
Stereochemical considerations lead to the view that a chain containing five (and ten) carbon (or carbon and oxygen) atoms would have all but returned on itself and completed one (or two) turn of a spiral.

(For a consideration of similar cases see Pickard, Kenyon, and Hunter, J., 1923, **123**, 1).

One of the most difficult of the unsolved problems in terpene chemistry is the relation between borneol and *iso*borneol. The usually accepted formula of the latter is unsatisfactory in that it represents

$$\begin{array}{ccc} CH_2 & \!\!-CH- & \!\!CMe_2 \\ | & CH_2 & | \\ CH_2 & \!\!-CH- & \!\!C(OH)Me \end{array}$$
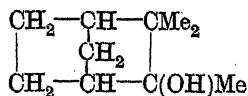
the compound as a tertiary alcohol. Numerous attempts have been made in this laboratory to prepare esters of tertiary alcohols by the method which has proved so satisfactory in the case of secondary alcohols, *i.e.*, by heating with acid anhydrides or by treatment with acid chlorides in pyridine solution, but in no single case has an ester been produced in sufficient quantity for isolation; the compound obtained in each case being an unsaturated hydrocarbon. When it is borne in mind that *iso*borneol, heated with phthalic

anhydride at 110—115° for several hours, is quantitatively converted into its hydrogen phthalate, the contrast between the behaviour of this alcohol and of tertiary alcohols as a class is most marked.

Moreover, many attempts have been made to effect the resolution of tertiary alcohols by the methods which have proved so successful in the case of secondary alcohols, but in no single case, as yet, has a tertiary alcohol containing the hydroxyl group attached to the asymmetric carbon atom been resolved. On the other hand, *iso*-borneol is resolved into its *d*- and *l*-forms by this method with the utmost ease and readiness. The results of the investigation here recorded lend support to the view that bornel and *iso*borneol are geometrical isomerides, a result which is also in harmony with the experimental work described in Part I (*loc. cit.*).

Another curious fact is that in the resolution of *cis*- and *trans*-isomerides by the acid-ester method a given alkaloid (as a rule) forms a less soluble salt with the acid ester of the *d*-form of the *cis*-isomeride and with the *l*-form of the *trans*, or *vice versa*. For example, strychnine forms a less soluble salt with the *d*-isomeride of " α " 2-methyl*cyclo*hexanol and with the *l*-isomeride of " β " 2-methyl*cyclo*hexanol : brucine forms a less soluble salt with *l*-menthol and with *d*-*neo*menthol. Similarly, strychnine (and *l*-menthylamine) forms a less soluble salt with *d*-*iso*borneol and with *l*-borneol. These results may be regarded as further support for the view that borneol and *iso*borneol are geometrical isomerides.

EXPERIMENTAL.

Pure *d*-fenchone was obtained from fennel oil by Gardner and Cockburn's method (J., 1898, **73**, 275); it distilled at 81°/18 mm. and set to a mass of white, prismatic needles at 5—6° : it had $[\alpha]_D^{20°} + 62.62°$ and $D_4^{20°}$ 0.9460. It readily gave an oxime which melted at 168° and possessed the following rotatory powers in 5% solution in benzene : $[\alpha]_{6708} + 63.7°$, $[\alpha]_{5893} + 86.8°$, $[\alpha]_{5780} + 91.6°$, $[\alpha]_{5461} + 105.4°$, $[\alpha]_{4359} + 191.4°$.

By the reduction of *d*-fenchone with sodium in boiling ethyl-alcoholic solution, a mixture of α- and β-fenchyl alcohols was obtained containing the components in the proportion of about 9 : 1. The proportion of the β-isomeride was not increased by any of the other methods of reduction which were tried.

α-*Fenchyl alcohol* was separated from this mixture by the following method. The mixture was heated with phthalic anhydride (1 mol.) at 115—120° for 12 hours, and the product worked up in the usual manner. Previous to any crystallisation, the mixture of fenchyl hydrogen phthalates melted at 136—140° and had

$[\alpha]_D + 19 \cdot 4°$ in 5% ethyl-alcoholic solution. After six recrystallisations from glacial acetic acid, a constant rotatory power and a constant melting point were reached. This pure d-fenchyl hydrogen phthalate forms long, prismatic needles which melt at 146° and in 5% solution in ethyl alcohol give the following rotatory powers : $[\alpha]_{5893} + 21 \cdot 6°$, $[\alpha]_{5461} + 27 \cdot 0°$, $[\alpha]_{4359} + 65 \cdot 2°$.

These values were unaltered after the *strychnine* salt of the hydrogen phthalate had been crystallised from ethyl alcohol and subsequently decomposed (Found by titration : M, 302·3. Calc., M, 302).

It forms a *magnesium* salt which crystallises from aqueous alcohol in needles, m. p. 290—295° (*vide infra*). Hydrolysis of the hydrogen phthalate was effected by heating with aqueous caustic soda and removing the α-fenchyl alcohol in a current of steam.

α-Fenchyl alcohol distils at 94°/20 mm. and crystallises in long, stout prisms, m. p. 47°; it possesses an odour resembling that of camphor and somewhat sweeter than that of d-fenchone. The rotatory powers are given in Table I.

α-*Fenchyl* p-*nitrobenzoate*, prepared by the action of p-nitrobenzoyl chloride on the alcohol in pyridine solution, crystallises from alcohol or glacial acetic acid in pale yellow needles, m. p. 108—109°. It possesses the following rotatory powers in benzene and carbon disulphide (5% solutions), respectively : $[\alpha]_{6708}-13 \cdot 9°$ and $-16 \cdot 1°$; $[\alpha]_{5893}-17 \cdot 4°$ and $-20 \cdot 0°$; $[\alpha]_{5780}-18 \cdot 0°$ and $-21 \cdot 9°$; $[\alpha]_{5461}-19 \cdot 6°$ and $-23 \cdot 2°$; $[\alpha]_{4359}-29 \cdot 5°$ and $-35 \cdot 4°$.

α-*Fenchyl* p-*chlorobenzoate*, prepared in a similar manner, crystallises from alcohol in needles, m. p. 73—74° (Found by hydrolysis with alcoholic potassium hydroxide; M, 293. Calc., M, 292).

β-*Fenchyl Alcohol*.—The separation of β-fenchyl hydrogen phthalate from the acetic acid mother-liquors from which the α-fenchyl hydrogen phthalate had been incompletely removed proved to be extremely tedious by the process of fractional precipitation or crystallisation, and after many trials was abandoned. The whole of the hydrogen phthalates were therefore thrown out of solution by addition of water, and portions were converted into salts with different metals. It was hoped that fractional crystallisation of one of these would bring about the separation of the desired β-isomeride. The salt with magnesium appeared to be the most hopeful and the systematic fractional crystallisation of this was resorted to. The result, however, was to bring out as the least soluble fraction a magnesium salt which on decomposition yielded pure α-fenchyl hydrogen phthalate. The hydrogen phthalates were therefore recovered from the more soluble fractions of the magnesium salt and hydrolysed. The impure β-fenchyl alcohol thus obtained

was converted into the *p*-nitrobenzoate, m. p. 80—90°. This mixture of esters after four recrystallisations from glacial acetic acid gave a crop of crystals which melted at 108—109° and corresponded with α-fenchyl *p*-nitrobenzoate. The first two mother-liquors from this series of crystallisations were precipitated with excess of water, when a *p*-nitrobenzoate was obtained of $[α]_D + 7·0°$. This was largely the β-isomeride and after some eight crystallisations from ethyl alcohol pure β-fenchyl *p*-nitrobenzoate was obtained as clusters of pale yellow, feathery needles, m. p. 82—83° (Found : N, 4·7. Calc., N, 4·6%).

Specific Rotatory Powers of β*-Fenchyl* p*-Nitrobenzoate.*

Conc.	Solvent.	$[α]_{6708}$	$[α]_{5893}$	$[α]_{5780}$	$[α]_{5461}$	$[α]_{4359}$
5%	Benzene	+8·2°	+10·5°	+11·4°	+13·5°	+23·6°
5%	Carbon disulphide	10·3	13·5	14·8	17·7	28·4

This *p*-nitrobenzoate (70 g.) was hydrolysed by heating with alcoholic caustic potash (1 mol.) for ½ hour. β-Fenchyl alcohol distils at 91°/18 mm. and melts at 3—4° and shows $[α]_D - 23·28°$. Its odour is similar to that of α-fenchyl alcohol.

β-*Fenchyl hydrogen phthalate*, prepared by the method described above and crystallised twice from acetic acid, forms small, white needles which melt at 153° and give the following rotatory powers in 5% solution in ethyl alcohol : $[α]_{6708} + 7·5°$, $[α]_{5893} + 10·3°$, $[α]_{5780} + 11·3°$, $[α]_{5461} + 13·3°$, $[α]_{4359} + 26·3°$. On hydrolysis, this ester yielded β-fenchyl alcohol of unchanged rotatory power.

The oxidation of the α*-and* β*-fenchyl alcohols to fenchone was* effected by means of chromic acid mixture and the following results were obtained ($l = 25$ mm.) :

$$α_D^{20°}.$$

Fenchone from α-fenchyl alcohol, +14·77°.
,,   ,,   β-   ,,   ,,   14·64.
,,   ,,   original sample   14·81.

Each sample of fenchone was converted into the oxime and by the method of mixed melting-point determination found to be identical with the original *d*-fenchoneoxime of melting point 167—168°.

*l-iso*Borneol was readily obtained by the fractional crystallisation of the cinchonine salts of *dl-iso*bornyl hydrogen phthalate (Part I, *loc. cit.*) : these authors used the *l*-menthylamine salt of the hydrogen phthalate for the preparation of *d-iso*borneol, but we have found that the expensive *l*-menthylamine can be replaced with advantage by the more accessible strychnine. The partly active *d-iso*bornyl hydrogen phthalate recovered from the more

soluble portions of the cinchonine salt was dissolved in hot ethyl alcohol, and the calculated amount of strychnine added. After six or seven recrystallisations, the optically pure lB, dA salt was obtained as fine, glistening needles, m. p. 231—232°.

The rotatory powers of the d- and l-isoborneols are in excellent agreement with those given by the above-mentioned authors.

l-Borneol was prepared from natural borneol ($[\alpha]_D$ 36·0° in 5% ethyl-alcoholic solution) obtained from Schimmel, by crystallisation of the strychnine salt of l-bornyl hydrogen phthalate. After four crystallisations from ethyl alcohol, the optically pure lB, lA salt was obtained as fine crystalline needles, m. p. 202°. The rotatory power of the l-borneol thus obtained was identical with that quoted in Part I (*loc. cit.*).

Esters of the normal fatty acids with α- and β-fenchyl alcohols, d- and l-isoborneols and l-borneol were prepared by the usual methods. They are, for the most part, pleasant-smelling liquids the physical constants of which are given in the tables.

TABLE I.

Specific Rotatory Powers of the Esters in the Homogeneous State at 20°

		$D_4^{20°}$.	λ. 6708.	5893.	5780.	5461.	4359.
α-Fenchyl alcohol		0·9641	−9·83°	−12·88°	−13·48°	−15·04°	−26·14°
,,	formate	0·9902	57·07	75·36	78·84	89·67	151·98
,,	acetate	0·9695	48·34	63·74	66·82	75·73	128·93
,,	propionate	0·9614	45·87	60·47	63·30	71·62	121·63
,,	n-butyrate	0·9522	40·56	53·77	56·00	63·50	107·16
,,	n-valerate	0·9453	37·07	48·94	51·35	58·03	98·59
,,	n-hexoate	0·9400	35·70	47·38	49·30	55·98	95·87
,,	n-heptoate	0·9338	35·30	46·39	48·68	55·13	93·81
,,	n-octoate	0·9277	33·44	44·09	46·26	52·43	89·10
,,	n-nonoate	0·9235	30·21	39·85	41·65	47·17	80·35
,,	n-laurate	0·9160	27·21	36·35	38·25	43·17	74·06
,,	n-myristate	0·9092	26·62	34·98	36·74	41·57	70·83
β-Fenchyl alcohol		0·9605	17·55	23·28	24·40	27·97	48·37
,,	formate	0·9933	8·19	10·93	11·40	12·88	22·59
,,	acetate	0·9694	10·61	14·09	14·81	16·90	29·05
,,	propionate	0·9601	9·56	12·67	13·31	14·98	25·92
,,	n-butyrate	0·9531	5·67	7·47	7·95	9·17	15·74
l-Bornyl formate		1·0100	36·62	48·61	50·71	57·60	98·12
,,	acetate	0·9920	32·32	42·74	44·56	50·45	85·12
,,	propionate	0·9768	30·32	40·03	41·91	47·40	80·08
,,	n-butyrate	0·9674	28·55	37·44	39·36	44·65	75·24
,,	n-valerate	0·9574	27·34	35·93	37·35	42·39	71·40
d-isoBornyl formate		1·0136	+22·32	+29·46	+30·55	+34·87	+ 60·03
l- ,,	acetate	0·9905	−38·08	−50·18	−52·76	−59·67	−101·00
d- ,,	propionate	0·9798	+38·19	+50·21	+52·38	+59·48	+100·19
l- ,,	n-butyrate	0·9690	−37·41	−49·25	−51·23	−58·15	− 98·59
d- ,,	n-valerate	0·9592	+36·24	+48·00	+50·46	+56·98	+ 95·98

TABLE II.

Determinations of Rotatory Power in Various Solvents at 20° C. l = 200 mm.

Solute	Solvent	Grams of solute in 100 c.c. of solution	α_λ					[α]_λ				
			6708	5893	5780	5461	4359	6708	5893	5780	5461	4359
α-Fenchyl alcohol	Ethyl alcohol	5·01	−0·97°	−1·28°	−1·38°	−1·54°	−2·71°	−9·68°	−12·77°	−13·77°	−15·37°	−27·07°
,,	Carbon disulphide	5·00	0·42	0·58	0·61	0·67	1·11	4·20	5·80	6·10	6·70	11·10
,,	Benzene	5·00	0·45	0·62	0·66	0·76	1·38	4·50	6·20	6·60	7·60	13·80
β-Fenchyl alcohol	Ethyl alcohol	4·35	1·48	1·88	2·01	2·28	4·00	17·02	21·62	23·12	26·23	46·01
,,	Carbon disulphide	4·32	2·13	2·76	2·90	3·31	5·97	24·63	31·91	33·53	38·27	69·02
α-Fenchyl formate	Ethyl alcohol	5·00	−5·50	−7·24	−7·64	−8·65	−14·72	−55·00	−72·40	−76·40	−86·50	−147·20
,, acetate	,,	5·10	4·84	6·41	6·72	7·64	13·10	47·45	62·84	65·90	74·90	128·43
,, propionate	,,	5·00	4·41	5·83	6·22	6·98	11·83	44·00	58·23	62·13	69·72	118·16
,, n-butyrate	,,	5·02	3·81	5·06	5·34	6·01	10·37	37·95	50·40	53·19	59·86	103·29
,, n-valerate	,,	5·03	3·51	4·63	4·95	5·52	9·48	34·89	46·02	49·20	54·87	94·23
,, n-hexoate	,,	5·01	3·33	4·43	4·67	5·28	8·98	33·23	44·21	46·61	52·68	89·65
,, n-heptoate	,,	5·02	3·30	4·40	4·57	5·17	8·80	32·87	43·82	45·52	51·49	87·65
,, n-octoate	,,	5·00	3·05	4·11	4·25	4·83	8·28	30·50	41·10	42·50	48·30	82·80
,, n-nonoate	,,	5·00	2·72	3·65	3·79	4·27	7·32	27·17	36·46	37·86	42·66	73·13
,, n-laurate	,,	5·02	2·62	3·49	3·59	4·04	6·93	26·15	34·83	35·83	40·32	69·10
,, n-myristate	,,	5·02	2·41	3·24	3·31	3·73	6·45	23·98	32·24	32·94	37·11	64·18
,, formate	Carbon disulphide	5·02	−4·68	−6·20	−6·42	−7·28	−12·28	−46·61	−61·75	−63·94	−72·51	−122·3
,, acetate	,,	5·01	3·60	4·74	4·92	5·58	9·25	35·93	47·31	49·10	55·99	92·32
,, propionate	,,	5·00	3·32	4·35	4·50	5·09	8·50	33·20	43·50	45·40	50·90	85·00
,, n-butyrate	,,	5·00	2·83	3·85	4·08	4·62	7·70	28·30	38·50	40·80	46·20	77·00
,, n-valerate	,,	5·00	2·55	3·44	3·64	4·10	6·84	25·50	34·40	36·40	41·00	68·40
,, n-hexoate	,,	5·00	2·44	3·29	3·50	3·98	6·54	24·40	32·90	35·00	39·80	65·40
,, n-heptoate	,,	5·00	2·36	3·15	3·36	3·78	6·33	23·60	31·50	33·60	37·80	63·30
,, n-octoate	,,	6·00	2·22	2·89	3·10	3·49	5·90	22·18	28·87	30·97	34·87	58·94
,, n-nonoate	,,	5·00	1·98	2·61	2·82	3·18	5·37	19·80	26·10	28·20	31·80	53·70
,, n-laurate	,,	5·00	1·81	2·48	2·68	3·05	5·04	18·10	24·80	26·80	30·50	50·40
,, n-myristate	,,	5·00	1·68	2·25	2·45	2·78	4·64	16·80	22·50	24·50	27·80	46·40
β-Fenchyl formate	Ethyl alcohol	5·03	0·76	0·98	1·05	1·18	2·04	7·56	9·75	10·45	11·74	20·32
,, acetate	,,	5·05	0·82	1·12	1·21	1·40	2·41	8·13	11·10	12·00	13·88	23·89
,, propionate	,,	5·01	0·78	1·00	1·05	1·26	2·12	7·78	9·98	10·48	12·57	21·16
,, n-butyrate	,,	4·56	0·42	0·53	0·54	0·60	1·01	4·61	5·81	5·92	6·58	11·08
,, formate	Carbon disulphide	5·04	0·92	1·29	1·38	1·59	2·64	9·14	12·81	13·70	15·79	20·22

	Solvent											
β-Fenchyl acetate	Carbon disulphide	5·00	1·00	1·35	1·44	1·67	2·84	9·99	13·49	14·39	16·68	28·37
„ propionate	„	5·00	0·91	1·24	1·32	1·52	2·63	9·10	12·40	13·20	15·20	26·30
„ n-butyrate	„	4·33	0·46	0·60	0·67	0·77	1·38	5·31	6·93	7·74	8·89	15·94
l-Borneol	Ethyl alcohol	5·00	2·82	3·71	3·78	4·20	7·40	28·19	37·09	37·79	41·98	73·98
„	Carbon disulphide	5·32	3·18	4·13	4·28	4·88	8·23	31·80	41·30	42·80	48·80	82·30
l-isoBorneol	Ethyl alcohol	5·00	2·89	3·68	3·75	4·21	7·16	27·16	34·59	35·25	39·57	67·30
„	Carbon disulphide	5·10	1·92	2·39	2·45	2·72	4·60	19·20	23·98	24·43	27·19	45·99
l-Bornyl formate	Ethyl alcohol	5·03	3·59	4·77	4·83	5·48	9·48	35·18	46·75	47·34	53·70	92·91
„ acetate	„	5·03	3·56	4·72	4·80	5·38	9·24	34·90	46·27	46·96	52·75	90·59
„ propionate	„	5·05	3·24	4·24	4·39	5·02	8·48	32·21	42·15	43·64	49·91	84·31
„ n-butyrate	„	5·05	3·06	3·97	4·11	4·62	7·76	30·43	39·48	40·87	45·95	77·16
„ n-valerate	„	5·04	2·95	3·59	3·78	4·28	7·32	29·20	35·53	37·41	42·36	72·45
„ formate	Carbon disulphide	5·02	3·28	4·35	4·68	5·25	8·92	32·54	43·16	46·43	52·09	88·50
„ acetate	„	4·98	3·03	3·99	4·17	4·71	8·04	30·20	39·76	41·56	46·94	80·13
„ propionate	„	5·07	2·78	3·56	3·74	4·22	7·12	27·91	35·74	37·54	42·36	71·47
„ n-butyrate	„	5·01	2·53	3·22	3·44	3·92	6·72	24·93	31·73	33·90	38·63	66·22
„ n-valerate	„	5·08	2·46	3·17	3·27	3·72	6·32	24·56	31·65	32·64	37·14	63·10
d-isoBornyl formate	Ethyl alcohol	5·04	+4·04	+3·00	+3·15	+3·59	+5·96	+23·83	+29·54	+31·02	+35·35	58·69
l- „ acetate	„	5·01	-4·12	-5·35	-5·57	-6·22	-10·67	-40·10	-53·09	-55·28	-61·73	-105·9
d- „ propionate	„	4·98	+4·02	+5·47	+5·82	+6·51	+10·94	+41·13	+54·61	+58·10	+65·00	-109·2
l- „ n-butyrate	„	4·97	+4·02	-5·40	+5·50	+6·24	+10·57	+40·39	+54·25	+55·26	+62·69	-106·2
d- „ n-valerate	„			+5·23	+5·38	+6·07	+10·23	+40·26	+52·65	+54·16	+60·12	-104·1
d- „ formate	Carbon disulphide	5·02	+2·13	+2·71	-2·87	-3·23	-5·32	-21·22	-27·00	-28·59	-32·18	53·00
l- „ acetate	„	5·05	-3·70	-4·73	+4·99	+5·65	+9·59	+36·62	+46·81	+49·38	+55·91	94·91
d- „ propionate	„	5·00	+3·61	+4·66	+4·87	+5·50	+9·20	+36·08	+46·57	+48·67	+54·96	91·94
l- „ n-butyrate	„	4·99	-3·48	-4·50	-4·63	-5·32	-8·90	-34·85	-45·06	-46·25	-53·27	89·13
d- „ n-valerate	„	5·01	+3·41	+4·45	+4·60	+5·25	+8·75	+34·03	+44·40	+45·90	+52·38	87·10

TABLE III.

Photographic Determinations of Rotatory Power in the Homogeneous State at 20°.

" α "-Fenchyl formate.			" β "-Fenchyl alcohol.		
Wave-length. λ.	Obs. rot. power. (l=50 mm.).	Spec. rot. power. $[\alpha]_\lambda^{20°}$.	Wave-length. λ.	Obs. rot. power. (l=100 mm.).	Spec. rot. power. $[\alpha]_\lambda^{20°}$.
4156 Å.	− 85·00°	−171·68°	4337 Å.	−47·00°	−48·73°
4015 Å.	− 92·00	−185·84	4144 Å.	−53·00	−54·96
3913 Å.	− 99·00	−199·96	3978 Å.	−59·00	−61·18
3800 Å.	−106·00	−214·12	3836 Å.	−65·00	−67·40

TABLE IV.

Refractive Indices of the " α "-Fenchyl Esters.

Measured in a Pulfrich Refractometer at 20°.

Wave-length.	a-Fenchyl formate.	a-Fenchyl acetate.	a-Fenchyl propionate.	a-Fenchyl n-butyrate.	a-Fenchyl n-valerate.	a-Fenchyl n-hexoate.
6708 Å.	1·4582	1·4541	1·4528	1·4536	1·4551	1·4557
6402	1·4588	1·4549	1·4534	1·4544	1·4558	1·4563
6096	1·4601	1·4561	1·4547	1·4556	1·4570	1·4575
5896	1·4610	1·4570	1·4556	1·4564	1·4579	1·4585
5882	1·4606	1·4567	1·4552	1·4561	1·4576	1·4581
5790	1·4614	1·4573	1·4560	1·4568	1·4583	1·4589
5782	1·4615	1·4574	1·4561	1·4569	1·4584	1·4590
5700	1·4618	1·4577	1·4564	1·4572	1·4587	1·4593
5461	1·4629	1·4588	1·4576	1·4583	1·4598	1·4602
5218	1·4643	1·4602	1·4588	1·4596	1·4612	1·4617
5153	1·4647	1·4607	1·4594	1·4601	1·4616	1·4622
5106	1·4650	1·4610	1·4597	1·4603	1·4620	1·4626
4359	1·4713	1·4671	1·4658	1·4665	1·4681	1·4698
4046	1·4751	1·4710	1·4685	1·4703	1·4718	1·4736

Wave-length.	a-Fenchyl n-heptoate.	a-Fenchyl n-octoate.	a-Fenchyl n-nonoate.	a-Fenchyl laurate.	a-Fenchyl myristate.
6708 Å.	1·4563	1·4569	1·4576	1·4590	1·4608
6402	1·4570	1·4576	1·4583	1·4598	1·4613
6096	1·4582	1·4589	1·4596	1·4610	1·4626
5896	1·4591	1·4596	1·4603	1·4619	1·4635
5882	1·4588	1·4593	1·4604	1·4615	1·4630
5790	1·4595	1·4600	1·4606	1·4623	1·4638
5782	1·4596	1·4601	1·4607	1·4623	1·4637
5700	1·4598	1·4604	1·4601	1·4626	1·4642
5461	1·4610	1·4615	1·4621	1·4638	1·4654
5218	1·4624	1·4629	1·4635	1·4651	1·4666
5153	1·4628	1·4633	1·4640	1·4655	1·4671
5106	1·4632	1·4637	1·4644	1·4658	1·4674
4359	1·4694	1·4700	1·4704	1·4721	1·4738
4046	1·4732	—	—	1·4759	1·4777

TABLE IV *continued.*

Refractive Indices of the " β "-Fenchyl Esters at 20°.

Wave-length.	β-Fenchyl formate.	β-Fenchyl acetate.	β-Fenchyl propionate.	β-Fenchyl *n*-butyrate (at 17·5°).
6708 Å.	1·4594	1·4556	1·4543	1·4553
6402	1·4601	1·4563	1·4550	1·4561
6096	1·4613	1·4576	1·4562	1·4572
5896	1·4623	1·4584	1·4571	1·4580
5882	1·4619	1·4581	1·4568	1·4578
5790	1·4625	1·4588	1·4574	1·4585
5782	1·4625	1·4589	1·4575	1·4586
5700	1·4629	1·4591	1·4577	1·4589
5461	1·4640	1·4601	1·4589	1·4601
5218	1·4654	1·4616	1·4602	1·4613
5153	1·4658	1·4620	1·4607	1·4617
5106	1·4661	1·4624	1·4610	1·4621
4359	1·4724	1·4697	1·4672	1·4684
4046	1·4762	1·4735	1·4710	—

Refractive Indices of Bornyl and iso*Bornyl Esters at 20°*

Wave-length in Å.

Ester.	6708.	5896.	5790.	5461.	4359.
l-Bornyl formate	1·4661	1·4689	1·4693	1·4710	1·4795
,, acetate	1·4607	1·4634	1·4640	1·4656	1·4740
,, propionate	1·4583	1·4612	1·4617	1·4632	1·4715
,, *n*-butyrate	1·4584	1·4613	1·4618	1·4633	1·4716
,, *n*-valerate	1·4586	1·4615	1·4620	1·4635	1·4718
d-*iso*Bornyl formate	1·4678	1·4707	1·4712	1·4728	1·4814
l- ,, acetate	1·4606	1·4633	1·4639	1·4655	1·4738
d- ,, propionate	1·4590	1·4619	1·4624	1·4639	1·4723
l- ,, *n*-butyrate	1·4594	1·4623	1·4628	1·4643	1·4727
d- ,, *n*-valerate	1·4596	1·4625	1·4630	1·4645	1·4729

TABLE V.

Observations of Density ($D_{4°}^{t°}$) *and of Rotatory Power* ($\alpha_{50\ mm.}$) *of the Compounds in the Homogeneous State.*

(The densities were determined in a pyknometer of about 1·5 c.c. capacity.)

" α "-*Fenchyl alcohol,* b. p. 86°/14 mm.

All rotatory powers are negative.

$D_{4°}^{t°}$ 0·9226 at 62·5°, 0·9034 at 84°, 0·8817 at 103°, 0·8638 at 122°.

α_{6708} 4·31° at 59°, 4·20° at 75°, 4·23° at 92°, 4·38° at 113°, 4·47° at 125°.

α_{5893} 5·77° at 58°, 5·66° at 75°, 5·55° at 92°, 5·74° at 113°, 5·85° at 125°.

α_{5780} 6·11° at 57°, 5·95° at 75°, 5·97° at 92°, 6·07° at 113°, 6·24° at 125°.

α_{5461} 6·83° at 57°, 6·74° at 75°, 6·75° at 92°, 6·87° at 113°, 7·10° at 125°.

α_{4359} 12·01° at 57°, 11·81° at 75°, 11·90° at 92°, 11·95° at 113°, 12·28° at 125°.

" β "-*Fenchyl alcohol,* b. p. 83°/12 mm.

$D_{4°}^{t°}$ 0·9625 at 18°, 0·9333 at 50°, 0·8999 at 83·5°, 0·8618 at 124°.

α_{6768} 8·40° at 19°, 8·88° at 51°, 8·95° at 80°, 8·72° at 103°, 8·64° at 122°.

α_{5893} 11·13° at 19°, 11·63° at 51°, 11·72° at 80°, 11·41° at 103°, 11·32° at 122°.

α_{5780} 11·71° at 19°, 11·98° at 51°, 12·33° at 80°, 12·09° at 103°, 11·89° at 122°.

α_{5461} 13·41° at 19°, 13·59° at 51°, 13·96° at 80°, 13·68° at 103°, 13·45° at 122°.

α_{4359} 23·18° at 19°, 23·91° at 51°, 24·08° at 80°, 23·57° at 103°, 23·07° at 122°.

<center>TABLE V (*continued*).</center>

" a "-*Fenchyl formate*, b. p. 97°/21 mm.

$D_4^{t°}$ 0·9929 at 17°, 0·9568 at 59°, 0·9275 at 91°, 0·9076 at 114°.

a_{6708} 28·26° at 20°, 25·82° at 45°, 23·36° at 74°, 21·37° at 102·5°, 20·18° at 123°.

a_{5893} 37·31° at 20°, 34·27° at 45°, 31·04° at 74°, 28·36° at 102·5°, 26·65° at 123°.

a_{5780} 39·03° at 20°, 35·88° at 45°, 32·44° at 74°, 29·88° at 102·5°, 28·01° at 123°.

a_{5461} 44·39° at 20°, 40·87° at 45°, 36·94° at 74°, 33·97° at 102·5°, 31·71° at 123°.

a_{4359} 75·23° at 20°, 69·23° at 45°, 62·99° at 74°, 57·89° at 102·5°, 53·79° at 123°.

" a "-*Fenchyl acetate*, b. p. 99°/19 mm.

$D_4^{t°}$ 0·9725 at 17°, 0·9326 at 61·5°, 0·9041 at 92°, 0·8827 at 114°.

a_{6708} 28·82° at 14°, 21·42° at 52·5°, 19·44° at 87·5°, 18·54° at 102°, 17·23° at 129°.

a_{5893} 31·41° at 14°, 28·25° at 52·5°, 25·63° at 87°, 24·43° at 102·5°, 22·71° at 129°.

a_{5780} 32·95° at 14°, 29·49° at 52·5°, 26·77° at 87·5°, 25·72° at 102·5°, 23·87° at 129°.

a_{5461} 37·36° at 14°, 33·42° at 52·5°, 30·21° at 87·5°, 28·94° at 103°, 26·95° at 130°.

a_{4359} 63·60° at 14°, 56·90° at 52·5°, 51·65° at 87°, 49·17° at 102·5°, 45·66° at 128·5°.

" a "-*Fenchyl propionate*, b. p. 115°/21 mm.

$D_4^{t°}$ 0·9565 at 14°, 0·9302 at 56°, 0·9080 at 83°, 0·8802 at 111°.

a_{6708} 22·05° at 20°, 20·04° at 47·5°, 18·60° at 73°, 17·40° at 95·5°, 16·25° at 120°.

a_{5893} 29·07° at 20°, 26·42° at 47·5°, 24·57° at 73°, 23·00° at 95·5°, 21·47° at 120°.

a_{5780} 30·43° at 20°, 27·61° at 47·5°, 25·85° at 73°, 23·95° at 95·5°, 22·32° at 120°.

a_{5461} 34·43° at 20°, 31·35° at 47·5°, 29·34° at 73°, 27·21° at 95·5°, 25·23° at 120°.

a_{4359} 58·47° at 20°, 52·82° at 47·5°, 49·34° at 73°, 45·95° at 95°, 42·88° at 120°.

" a "-*Fenchyl n-butyrate*, b. p. 127°/21 mm.

$D_4^{t°}$ 0·9607 at 10°, 0·9279 at 48°, 0·9072 at 73·5°, 0·8736 at 111°.

a_{6708} 19·31° at 20°, 17·54° at 52°, 15·88° at 87°, 15·20° at 103°, 14·27° at 123°.

a_{5893} 25·60° at 20°, 23·15° at 52°, 20·88° at 87°, 20·04° at 103°, 18·81° at 123°.

a_{5780} 26·66° at 20°, 24·16° at 52°, 21·78° at 87°, 20·90° at 103°, 19·75° at 123°.

a_{5461} 30·23° at 20°, 27·44° at 52°, 24·69° at 87°, 23·66° at 103°, 22·22° at 123°.

a_{4359} 51·02° at 20°, 46·78° at 52°, 42·45° at 87°, 40·14° at 103°, 37·83° at 123°.

" a "-*Fenchyl n-valerate*, b. p. 135°/15 mm.

$D_4^{t°}$ 0·9517 at 12·5°, 0·9141 at 57°, 0·8948 at 81°, 0·8754 at 103°.

a_{6708} 17·56° at 19°, 16·37° at 46·5°, 14·83° at 80°, 13·93° at 103°, 13·00° at 125°.

a_{5893} 23·19° at 19°, 21·67° at 46·5°, 19·60° at 80°, 18·40° at 103°, 17·11° at 125°.

a_{5780} 24·32° at 19°, 22·77° at 46·5°, 21·03° at 80°, 19·52° at 103°, 18·26° at 125°.

a_{5461} 27·48° at 19°, 25·79° at 46·5°, 23·59° at 80°, 21·87° at 103°, 20·51° at 125°.

a_{4359} 46·72° at 19°, 43·62° at 46·5°, 39·28° at 80°, 36·57° at 103°, 34·42° at 125°.

TABLE V (*continued*).

" *a* "-*Fenchyl* n-*hexoate*, b. p. 152°/17 mm.

$D_{4°}^{t°}$	0·9471 at 11·5°, 0·9194 at 45°, 0·8983 at 69°, 0·8632 at 112°.
a_{6708}	16·78° at 20°, 15·45° at 49°, 14·02° at 81°, 13·03° at 103°, 12·03° at 123°.
a_{5893}	22·27° at 20°, 20·64° at 49°, 18·63° at 81°, 17·40° at 103°, 16·32° at 123°.
a_{5780}	23·17° at 20°, 21·47° at 48°, 19·56° at 81°, 18·27° at 103°, 17·12° at 123°.
a_{5461}	26·31° at 20°, 24·35° at 48°, 22·09° at 81°, 20·77° at 103°, 19·24° at 123°.
a_{4359}	45·06° at 20°, 41·40° at 49°, 37·56° at 81°, 34·85° at 103°, 32·50° at 123°.

" *a* "-*Fenchyl* n-*heptoate*, b. p. 160°/16 mm.

$D_{4°}^{t°}$	0·9428 at 8·5°, 0·9097 at 50°, 0·8868 at 79°, 0·8630 at 107°.
a_{6708}	16·69° at 16°, 14·76° at 53·5°, 13·15° at 93°, 12·17° at 121°.
a_{5893}	22·00° at 16°, 19·41° at 53·5°, 17·10° at 95°, 15·83° at 121°.
a_{5780}	23·03° at 16°, 20·33° at 53·5°, 18·11° at 94°, 16·58° at 122°.
a_{5461}	26·04° at 16°, 23·09° at 53·5°, 20·53° at 92°, 18·81° at 122°.
a_{4359}	44·34° at 16°, 39·29° at 54°, 34·55° at 93·5°, 31·75° at 123°.

" *a* "-*Fenchyl* n-*octoate*, b. p. 176°/25 mm.

$D_{4°}^{t°}$	0·9332 at 13·5°, 0·8941 at 63°, 0·8770 at 83°, 0·8539 at 113°.
a_{6708}	15·60° at 18°, 14·29° at 48°, 13·20° at 74°, 11·89° at 107°, 11·11° at 130°.
a_{5893}	20·57° at 18°, 18·76° at 49°, 17·40° at 74°, 15·76° at 107°, 14·70° at 130°.
a_{5780}	21·57° at 18°, 19·75° at 47°, 18·44° at 74°, 16·69° at 107°, 15·47° at 130°
a_{5461}	24·44° at 18°, 22·36° at 47°, 20·70° at 74°, 18·65° at 107°, 17·39° at 130°˙
a_{4359}	41·55° at 18°, 37·94° at 48°, 34·76° at 74°, 30·81° at 107°, 28·15° at 130°˙

" *a* "-*Fenchyl* n-*nonoate*, b. p. 185°/16 mm.

$D_{4°}^{t°}$	0·9287 at 13°, 0·8999 at 50·5°, 0·8788 at 78°, 0·8478 at 116°.
a_{6708}	14·18° at 15°, 12·51° at 52·5°, 11·02° at 91°, 10·12° at 113°, 9·73° at 132°.
a_{5893}	18·68° at 15°, 16·46° at 52·5°, 14·44° at 91°, 13·30° at 113°, 12·57° at 132°.
a_{5780}	19·54° at 15°, 17·27° at 52·5°, 15·22° at 91°, 14·10° at 113°, 13·42° at 132°.
a_{5461}	22·09° at 15°, 19·53° at 52·5°, 17·17° at 91°, 15·92° at 113°, 15·12° at 132°.
a_{4359}	37·65° at 15°, 33·40° at 52·5°, 29·79° at 91°, 27·62° at 113°, 26·21° at 132°.

" *a* "-*Fenchyl laurate*, b. p. 207—209°/14 mm.

$D_{4°}^{t°}$	0·9188 at 15·5°, 0·8906 at 53°, 0·8714 at 78·5°, 0·8466 at 110°.
a_{6708}	12·73° at 12°, 11·41° at 50°, 10·83° at 77°, 10·25° at 98°, 9·39° at 119·5°.
a_{5893}	17·05° at 12°, 15·09° at 50°, 13·93° at 77°, 13·30° at 97°, 12·48° at 119·5°.
a_{5780}	17·91° at 12°, 15·96° at 50°, 14·58° at 77°, 13·92° at 98°, 12·91° at 121°.
a_{5461}	20·24° at 12°, 18·02° at 50°, 16·49° at 77°, 15·68° at 99°, 14·56° at 121·5°.
a_{4359}	34·75° at 12°, 31·03° at 50°, 28·52° at 77°, 26·72° at 98°, 25·15° at 118°.

" *a* "-*Fenchyl myristate*, b. p. 190—195°/2 mm.

$D_{4°}^{t°}$	0·9121 at 16°, 0·8849 at 53°, 0·8630 at 82°, 0·8453 at 105°.
a_{6708}	12·14° at 19·5°, 10·73° at 60°, 9·53° at 87·5°, 9·17° at 104·5°, 8·57° at 127°.
a_{5893}	15·93° at 19·5°, 13·88° at 60°, 12·62° at 86·5°, 11·92° at 104·5°, 11·12° at 128°.
a_{5780}	16·67° at 20·5°, 14·58° at 59°, 13·43° at 86°, 12·80° at 104°, 11·74° at 127°.
a_{5461}	18·71° at 22·5°, 16·56° at 59°, 15·15° at 86·5°, 14·48° at 104°, 13·35° at 127·5°.
a_{4359}	32·27° at 19·5°, 28·16° at 60°, 25·86° at 86·5°, 24·36° at 107°, 22·87° at 127·5°.

<div align="center">TABLE V (<i>continued</i>).</div>

" β "-<i>Fenchyl formate</i>, b. p. 83·5°/11 mm.

$D_{4°}^{t°}$ 0·9945 at 18·5°, 0·9634 at 52·5°, 0·9363 at 82·5°, 0·9016 at 118°.
a_{6708} 4·05° at 19·5°, 3·74° at 51·5°, 3·53° at 74°, 3·25° at 96°, 3·06° at 117°.
a_{5893} 5·44° at 19·5°, 4·91° at 51·5°, 4·59° at 74°, 4·29° at 95°, 4·03° at 117°.
a_{5780} 5·67° at 19·5°, 5·02° at 51·5°, 4·75° at 74·5°, 4·43° at 95°, 4·19° at 116·5°.
a_{5461} 6·41° at 19·5°, 5·71° at 51·5°, 5·31° at 74·5°, 4·98° at 95°, 4·67° at 116·5°.
a_{4359} 11·23° at 19·5°, 10·15° at 51·5°, 9·39° at 74·5°, 8·89° at 94°, 8·35° at 116°.

-<i>Fenchyl acetate</i>, b. p. 90°/12 mm.

$D_{4°}^{t°}$ 0·9739 at 15°, 0·9397 at 53·5°, 0·9162 at 81°, 0·8906 at 110°.
a_{6708} 5·17° at 18·5°, 4·90° at 49°, 4·48° at 76°, 4·13° at 97°, 3·89° at 114·5°.
a_{5893} 6·85° at 18·5°, 6·38° at 49·5°, 5·88° at 75°, 5·50° at 97°, 5·16° at 114·5°.
a_{5780} 7·25° at 18·5°, 6·57° at 49°, 5·88° at 74°, 5·80° at 97·5°, 5·35° at 114·5°.
a_{5461} 8·23° at 18·5°, 7·48° at 49°, 6·75° at 74°, 6·51° at 97·5°, 6·03° at 114·5°.
a_{4359} 14·14° at 18·5°, 12·95° at 49·5°, I1·87° at 75°, 11·35° at 97°, 10·55° at
            114·5°.

-<i>Fenchyl propionate</i>, b. p. 102°/11 mm.

$D_{4°}^{t°}$ 0·9614 at 18·5°, 0·9334 at 52°, 0·9059 at 81·5°.
a_{6708} 4·61° at 18°, 4·25° at 44°, 3·95° at 74°, 3·64° at 102°, 3·32° at 125°.
a_{5893} 6·11° at 18°, 5·67° at 44°, 5·16° at 73·5°, 4·70° at 102°, 4·21° at 125°.
a_{5780} 6·42° at 18°, 6·04° at 44°, 5·43° at 74°, 5·08° at 102°, 4·53° at 126·5°.
a_{5461} 7·22° at 18°, 6·74° at 44·5°, 6·04° at 74°, 5·61° at 102·5°, 4·98° at 128°.
a_{4359} 12·51° at 18°, 11·69° at 43·5°, 10·62° at 75·5°, 9·70° at 102·5°, 8·89° at
            125°.

" β "-<i>Fenchyl</i> n-<i>butyrate</i>, b. p. 112°/16 mm., $D_{4°}^{20°}$ 0·9531.

	λ.			
6708.	5896.	5780.	5461.	4359.
−2·70°	−3·56°	−3·79°	−4·37°	−7·50°

<div align="center"><i>Esters of</i> 1-<i>Borneol.</i> $a_\lambda^{20°}$ (<i>l</i>=50 mm.).</div>

	B. p.	λ.				
	Mm.	6708.	5893.	5780.	5461.	4359.
l-Borny formate	94°/14	−18·49°	−24·55°	−25·61°	−29·09°	−49·55'
acetate	103°/14	16·03	21·15	22·10	25·02	42·22
propionate	114°/12	14·81	19·55	20·47	23·15	39·11
n-butyrate	125°/15	13·81	18·11	19·04	21·60	36·39
n-valerate	136°/12	13·09	17·20	17·88	20·20	34·18

<div align="center"><i>Esters of</i> iso<i>Borneol.</i> $a_\lambda^{20°}$ (<i>l</i>=50 mm.).</div>

	B. p.	λ.				
	Mm.	6708.	5893.	5780.	5461.	4359.
d-isoBornyl formate	94°/15	−11·31°	−14·93°	−15·48°	−17·63°	−30·42°
l- ,, acetate	112°/17	18·86	24·85	26·13	29·55	50·02
d- ,, propionate	119°/16	18·71	24·60	25·66	29·14	49·08
l- ,, n-butyrate	125°/14	18·08	23·86	24·82	28·17	47·76
d- ,, n-valerate	138°/14	17·38	23·02	24·20	27·33	46·03

aid of which some of the materials used in this investigation were purchased, and also to the Department of Scientific and Industrial Research for a grant which enabled one of them (H. E. M. P.) to participate in the work.

NOTES.

The Atomic Volume of Manganese.   By ALAN N. CAMPBELL.

THE curve of atomic volumes, plotted by means of the usually accepted values of the densities, shows in the neighbourhood of manganese two minima, one at manganese and the other at cobalt, with iron occupying a maximum between. With the new value for the density of manganese (Campbell, J., 1923, **123**, 2323), the two minima persist, but the first minimum is shifted from manganese to chromium.

|	V.	Cr.	Mn.	Fe.	Ni.	Co.	Cu.
At. wts.............	51·0	52·0	54·9	55·8	58·7	59·0	63·6
At. vols.	9·26	7·55	7·34 (old value)	7·46	6·65	6·59	7·1
			7·76 (new value)				

If the accepted value of the density of chromium should prove to be too high, the atomic volume of chromium would probably cease to be a minimum, and only one minimum would exist at cobalt, as is the case in all the other loops of the atomic-volume curve. —[*Received, March 30th, 1925.*]

Molybdenum   Pentoxide.   By WILLIAM WARDLAW and FRANK HAROLD NICHOLLS.

VARIOUS oxides intermediate between the dioxide and trioxide of molybdenum have been described. These substances, such as Mo_4O_{11}, Mo_3O_8, and Mo_5O_{12}, were investigated by Guichard (*Compt. rend.*, 1899, **129**, 722), who, finding that in every case sufficient purification with ammonia and hydrochloric acid left molybdenum dioxide, concluded that no homogeneous oxide between MoO_2 and MoO_3 exists. On the other hand, Smith and Oberholtzer (*Z. anorg.*

Chem., 1893, **4**, 236), by prolonged heating of the trioxide at 105—120° in dry hydrogen iodide, obtained a violet-blue product, $Mo_2O_5,1\cdot5H_2O$, which was stable in air but was completely dehydrated at a red heat, yielding a brown substance, Mo_2O_5. Again, the hydroxide, $MoO(OH)_3$, obtained by the action of ammonia on ammonium molybdenyl chloride, $MoOCl_3,2NH_4Cl$ (Klason, *Ber.*, 1901, **31**, 148), leaves, when cautiously heated in a stream of carbon dioxide, a violet-black powder which is soluble in sulphuric and hydrochloric acids with a difficulty varying with its temperature of preparation. It has the formula Mo_2O_5 and, according to Klason, is but slightly contaminated with trioxide and dioxide. So-called alkali salts of molybdenum pentoxide, $(NH_4)Mo_2O_5,3H_2O$, $NaMo_2O_5,3H_2O$, $BaMo_2O_5,3H_2O$, have been described by Mawrow and Nikolow (*Z. anorg. Chem.*, 1915, **92**, 138). It is difficult to see how these compounds can be regarded as derivatives of Mo_2O_5.

Pure molybdenum pentoxide is readily prepared by carefully heating the oxysulphate (J., 1924, **125**, 1910) or the oxyoxalate (this vol., p. 1311) of tervalent molybdenum in a current of nitrogen:

$$Mo_2O(SO_4)_2 = Mo_2O_5 + 2SO_2. \quad Mo_2O(C_2O_4)_2 = Mo_2O_5 + 4CO.$$
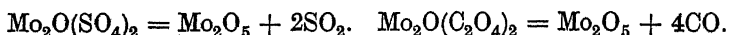
The molybdenum content of the violet-black residue was determined by dissolving a weighed quantity in acid, precipitating the molybdenum as sulphide, and igniting to the trioxide (Found : Mo, 70·4. Mo_2O_5 requires Mo, 70·6%).

The pentoxide remained almost unchanged (Found : Mo, 70·4%) after being boiled with five successive portions of ammonium hydroxide, washed with distilled water, and dried at 110°; were Guichard's conclusion correct, the product should have been more or less pure molybdenum dioxide. That the ammonia was not without action, however, was proved by the formation of molybdenum-blue when the ammoniacal extract was acidified and treated with hydrogen sulphide.

Like Klason's product, the pentoxide is difficultly soluble in hydrochloric and sulphuric acids.—UNIVERSITY OF BIRMINGHAM. [*Received, March 31st, 1925.*]

Chlorobenzthiazole Dibromide. By ROBERT FERGUS HUNTER.

Two grams of 1-chlorobenzthiazole (prepared according to Hofmann, *Ber.*, 1879, **12**, 1126, with the modification that the phenylthiocarbimide and phosphorus pentachloride were heated under reflux at 160—170° instead of in a sealed tube) were dissolved in 10 c.c. of chloroform and slowly treated with 2 c.c. of bromine. The solution, on being concentrated and cooled, furnished orange-red

in agreement with the figure given by Battegay and Claudin (*Bull. Soc. Ind. Mulhouse*, 1920, **86**, 632; *Bull. Soc. chim.*, 1921, **29**, 1017) and Grandmougin (*Compt. rend.*, 1921, **173**, 839), who synthesised it by another method, whereas K. H. Meyer and Zahn (*loc. cit.*) give 269—270°.

9 : 10-Dibromoanthracene tetrabromide when suspended in cold pyridine loses both bromine and hydrogen bromide, and the resulting 2 : 9 : 10-tribromo- and 2 : 3 : 9 : 10-tetrabromo-anthracene can be separated by fractional crystallisation from amyl alcohol.—The SIR JOHN CASS TECHNICAL INSTITUTE, Jewry Street, Aldgate, London. [*Received, May 14th, 1925.*]

The Reduction of Anethole Nitrosochloride by Stannous Chloride and Hydrochloric Acid. By JOHN BALDWIN SHOESMITH and ROBERT HENRY SLATER.

TWENTY grams of anethole nitrosochloride (see Orndorff and Morton, *Amer. Chem. J.*, 1900, **23**, 181) in 150 c.c. of chloroform (the only solvent in which the nitrosochloride is appreciably soluble) were vigorously stirred with 150 g. of stannous chloride dissolved in 200 c.c. of concentrated hydrochloric acid. The emulsion became transparent and yellow whilst its temperature gradually rose to 50°. After ½ hour's stirring, a yellow solid was precipitated and after 6 hours, precipitation was complete, the temperature of the mixture being that of the room. After filtration, the solid was dried over calcium chloride and potassium hydroxide, and unchanged nitroso-chloride extracted with chloroform. The residue (m. p. 259° with decomp.) was the double compound of *anisylideneazine hydrochloride* and *stannic chloride*, (MeO·C$_6$H$_4$·CH:N·N:CH·C$_6$H$_4$·OMe,HCl)$_2$,SnCl$_4$ (Found : Cl, 24·7; Sn, 13·1. C$_{32}$H$_{34}$O$_4$N$_4$Cl$_6$Sn requires Cl, 24·45; Sn, 13·6%), which with water was decomposed into stannic oxide and anisylideneazine, m. p. 168° (to a liquid crystal which was converted into the isotropic liquid at 180°) (Found : N, 10·8. Calc., N, 10·45%). Anisylideneazine acts as a mono-acid base, and in solution in chloroform is converted by hydrogen chloride into *anisylideneazine hydrochloride*, MeO·C$_6$H$_4$·CH:N·N:CH·C$_6$H$_4$·OMe,HCl, fine, yellow needles, m. p. 172°, which decompose at 177° (Found : Cl, 11·7. C$_{16}$H$_{17}$O$_2$N$_2$Cl requires Cl, 11·6%) and give anisaldehyde with nitrous acid and the above double compound with stannic chloride.

Oxidations in Turpentine and Olive Oil. By ERNEST WALKER.

A SIMPLE and useful method for the oxidation of organic compounds has been based on the property of turpentine of acquiring oxidising power by exposure to the air for some time. For example, diphenyl-chloroarsine, or diphenylarsenious oxide, was dissolved in a slight excess of turpentine (which had been thus exposed), and a trace of water added to promote hydrolysis. After a few hours, diphenyl-arsinic acid separated, m. p. 172° (after recrystallisation from water). In a similar manner, but without the addition of water, ββ′-dichlorodiethyl sulphide was converted into ββ′-dichlorodiethyl sulphoxide, m. p. 109° (after crystallisation from alcohol). Freshly distilled turpentine is quite inactive, but gradually acquires oxidising properties on standing.

Another medium which effects precisely similar oxidations is rancid olive oil. An old specimen of olive oil which has been much exposed to the air is usually sufficiently rancid for the purpose. Otherwise, fresh olive oil can be made rancid by bubbling air through it at about 70° for 24 hours. It is not sufficient for the olive oil simply to contain free fatty acid. Decomposition of the oil must be avoided and the correct degree of rancidity may be gauged by the change in colour of the oil from yellow to a pale green or almost colourless hue. The oil may then be said to be "activated." There can be little doubt that its oxidising properties are due to the presence of peroxides, analogous to those found in exposed turpentine, and that the decoloration of the oil represents the oxidising action of such per-oxides upon the pigment present. The products obtained by means of this reagent and by means of turpentine differ only in crystalline form. All three of the preceding substances were oxidised in a similar manner by rancid olive oil. The two arsenic compounds (which are solids) were dissolved in chloroform, and an equal volume of "activated" olive oil was added; in each case diphenylarsinic acid crystallised on standing. In the case of ββ′-dichlorodiethyl sulphide it was found possible greatly to accelerate the oxidation by bubbling air through the solution in the olive oil at 70°. The sulphoxide then commenced to crystallise in the course of a few minutes.—DEPARTMENT OF BIOCHEMISTRY, OXFORD. [*Received, May 11th, 1925.*]